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Report Title

Molecular Rotors

ABSTRACT

Most mechanical machines contain rotating parts and it is likely that the nanomachines of the future will be no exception. We proposed to find out how rotors 1-2 nm in size can be synthesized and attached to surfaces, and what their fundamental properties are. We studied their equilibrium behavior and driven response, the effects of rotational barriers and friction, and mutual and environmental interactions with potential future applications in mind in areas as diverse as molecular transistors, extremely compact microwave signal processing components, and micro-fluidic devices.

The projected involved the preparation, surface mounting, and characterization of single molecular rotors with both vertical and horizontal shafts, and both with and without large dipole moments. Our basic device is a surface mounted molecular dipolar rotor that has a base or bases that attach covalently to a flat insulating surface and support an axle oriented either perpendicularly to the surface by a single base, which in turn support a balanced 1–2 nm diameter rotor portion with a large in-plane electric dipole moment or support an axle oriented parallel to the surface by two bases and a similar rotor. The bearing consists of a single covalent bond, a fundamental element of molecular-scale mechanics.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

- [1] M. C. Hersam, "Monitoring and analyzing nonlinear dynamics in atomic force microscopy," *Small*, 2, 1122 (2006).
- [2] R. Basu, J. D. Tovar, and M. C. Hersam, "Scanning tunneling microscopy study of single molecule motion on the Si(100)-2×1 surface," *J. Vac. Sci. Technol. B*, 23, 1785 (2005).
- [3] N. P. Guisinger, N. L. Yoder, and M. C. Hersam, "Probing charge transport at the single molecule level on silicon by using cryogenic ultra-high vacuum scanning tunneling microscopy," *Proc. Nat. Acad. Sci.*, 102, 8838 (2005).
- [4] E. T. Foley, N. L. Yoder, N. P. Guisinger, and M. C. Hersam, "Cryogenic variable temperature ultra-high vacuum scanning tunneling microscope for single molecule studies on silicon surfaces," *Rev. Sci. Instrum.*, 75, 5280 (2004).
- [5] R. Basu, N. P. Guisinger, M. E. Greene, and M. C. Hersam, "Room temperature nanofabrication of atomically registered heteromolecular organosilicon nanostructures using multistep feedback controlled lithography," *Appl. Phys. Lett.*, 85, 2619 (2004).
- [6] A. S. Baluch, N. P. Guisinger, and M. C. Hersam, "Negative differential resistance through individual organic molecules bound to the Si(111)-7×7 surface," *TMS Lett.*, 1, 125 (2004).
- [7] M. C. Hersam and R. G. Reifenberger, "Charge transport through molecular junctions," *MRS Bull.*, 29, 385 (2004).
- [8] N. P. Guisinger, R. Basu, M. E. Greene, A. S. Baluch, and M. C. Hersam, "Observed suppression of room temperature negative differential resistance in organic monolayers on Si(100)," *Nanotechnology*, 15, S452 (2004).
- [9] M. E. Greene, N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, "Nitroxyl free radical binding to Si(100): A combined STM and computational modeling study," *Surface Science*, 559, 16 (2004).
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- [11] N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance through individual molecules on silicon surfaces," *Nano Letters*, 4, 55 (2004).
- [12] B. Wang, X. Zheng, J. Michl, E. T. Foley, M. C. Hersam, A. Bilić, M. J. Crossley, J. R. Reimers, and N. S. Hush, "An azanorbornadiene anchor for molecular-level construction on silicon(100)," *Nanotechnology*, 15, 324 (2004).
- [13] N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, "Molecular electronics on silicon: An ultra-high vacuum scanning tunneling microscopy study," *Ann. N. Y. Acad. Sci.*, 1006, 227 (2003).
- [14] Robert D. Horansky, Laura I. Clarke, Erick B. Winston, John C. Price, Steven D. Karlen, Peter D. Jarowski, Rosa Santillan, and Miguel A. Garcia-Garibay, "Dipolar rotor-rotor interactions in a difluorobenzene molecular rotor crystal" *Physical Review B* 74, 111629 (2006).
- [15] Robert Horansky, Laura I. Clarke, John C. Price, Tinh-Alfredo V. Khuong, Peter D. Jarowski, and Miguel A. Garcia-Garibay, "Dielectric Response of a Dipolar Molecular Rotor Crystal" *Physical Review B* 72, 014302 (2005).
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Number of Papers published in peer-reviewed journals: 33.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

[1] M. C. Hersam, "Introduction to nanometer scale science and technology," presented orally by M. C. Hersam at the Harold Washington College Nanoscience Seminar Series, Chicago, Illinois (10/5/06).

[2] M. C. Hersam, "Probing chemistry and electronic structure at the single molecule level with scanning tunneling microscopy," presented orally by M. C. Hersam at the Tufts University Department of Chemistry Colloquium, Medford, Massachusetts (10/3/06).

[3] M. C. Hersam, "Electrical contacts at the nanometer scale," presented orally by M. C. Hersam at the 52nd IEEE Holm Symposium, Montreal, Canada (9/27/06).

[4] M. C. Hersam, "Probing the dynamics of individual molecules on silicon surfaces with ultra-high vacuum scanning tunneling microscopy," presented orally by M. C. Hersam at the ACS Fall Meeting, San Francisco, California (9/11/06).

[5] M. C. Hersam, "Probing molecular electronics with scanning probe microscopy," presented orally by M. C. Hersam at the National Science Foundation Summer Institute on Micro and Nano Devices with Applications to Biology and Nanoelectronics, Evanston, Illinois (8/10/06).

[6] M. C. Hersam, "Nanoelectronics: Device physics and fabrication technology," presented orally by M. C. Hersam at the National Science Foundation Summer Institute on Micro and Nano Devices with Applications to Biology and Nanoelectronics, Evanston, Illinois (8/10/06).

[7] M. C. Hersam, "Ultra-high vacuum scanning tunneling microscopy studies of single molecules on semiconductor surfaces," presented orally by M. C. Hersam at the International Conference on Nanoscience and Technology, Basel, Switzerland (8/2/06).

[8] N. P. Guisinger and M. C. Hersam, "Chemistry and charge transport properties of organics on silicon," presented orally by N. P. Guisinger at the Telluride Workshop on Functional Modification of Semiconductor Surfaces, Telluride, Colorado (8/2/06).

[9] N. L. Yoder and M. C. Hersam, "Scanning probe microscopy: Delineating structure-property-processing relationships in hybrid organic/inorganic nanomaterials," presented orally by N. L. Yoder at the Microscopy and Microanalysis Meeting, Chicago, Illinois (8/1/06).

[10] M. C. Hersam, "Assessing the prospects and limitations of silicon-based molecular electronics with ultra-high vacuum scanning tunneling microscopy," presented orally by M. C. Hersam at the Molecular Conductivity and Sensor Workshop, Charlottesville, Virginia (7/27/06).

[11] M. C. Hersam, "Introduction to nanoelectronics," presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, St. Paul, Minnesota (7/13/06).

[12] M. C. Hersam, "Probing organic chemistry on silicon surfaces at the single molecule level with ultra-high vacuum scanning tunneling microscopy," presented orally by M. C. Hersam at the University of California at Riverside Chemistry Department Colloquium, Riverside, California (6/7/06).

[13] M. C. Hersam, "Probing the performance and reliability of silicon-based molecular electronic devices with ultra-high vacuum scanning tunneling microscopy," presented orally by M. C. Hersam at the 3rd Annual Foundations of Nanoscience Conference, Snowbird, Utah (4/24/06).

[14] M. C. Hersam, "Assessing the prospects and limitations of silicon-based molecular electronics with ultra-high vacuum scanning tunneling microscopy," presented orally by M. C. Hersam at the University of Illinois at Urbana-Champaign Materials Science and Engineering Department Colloquium, Urbana, Illinois (4/17/06).

[15] N. P. Guisinger, N. L. Yoder, R. Basu, and M. C. Hersam, "Silicon-based molecular electronics," presented orally by N. P. Guisinger at the ACS Spring Meeting, Atlanta, Georgia (3/28/06).

[16] M. C. Hersam, "Atomic resolution patterning of organosilicon heteromolecular nanostructures using feedback controlled lithography," presented orally by M. C. Hersam at the ACS Spring Meeting, Atlanta, Georgia (3/26/06).

[17] M. C. Hersam, "Molecular-scale patterning and characterization of organic structures on silicon," presented orally by M. C. Hersam at

the Joint International Conference on New Phenomena in Mesoscopic Systems and Surfaces and Interfaces of Mesoscopic Devices, Maui, Hawaii (12/2/05).

[18] M. C. Hersam, "Probing silicon-molecule junctions with scanning tunneling microscopy," presented orally by M. C. Hersam at the Materials Research Society Fall Meeting, Boston, Massachusetts (11/29/05).

[19] M. C. Hersam, "Directed assembly and characterization of organosilicon nanostructures using scanning tunneling microscopy," presented orally by M. C. Hersam at the International Symposium on Surface Science and Nanotechnology, Saitama, Japan (11/16/05).

[20] N. P. Guisinger, N. L. Yoder, and M. C. Hersam, "Probing silicon based molecular electronics with ultra-high vacuum scanning tunneling microscopy," presented orally by N. P. Guisinger at the 52nd AVS International Symposium, Boston, Massachusetts (11/3/05).

[21] R. Basu, J. D. Tovar, and M. C. Hersam, "Chemically engineering the motion of individual molecules on the Si(100)-2×1 surface: A scanning tunneling microscopy study," presented orally by R. Basu at the 52nd AVS International Symposium, Boston, Massachusetts (11/2/05).

[22] M. C. Hersam, "Nanoelectronics: Device physics and fabrication technology," presented orally by M. C. Hersam at the NanoCommerce/SEMI NanoForum, Chicago, Illinois (10/31/05).

[23] M. C. Hersam, "Hybrid organic/inorganic materials at the nanometer scale," presented orally by M. C. Hersam at the Golden Jubilee of Materials Science and Engineering, Evanston, Illinois (10/28/05).

[24] M. C. Hersam, "Hybrid organic/inorganic nanomaterials: Characterization, processing, and potential applications," presented orally by M. C. Hersam at the University of Pennsylvania Materials Science and Engineering Colloquium, Philadelphia, Pennsylvania (9/29/05).

[25] M. C. Hersam, "Probing single molecule charge transport on silicon surfaces using scanning tunneling microscopy," presented orally by M. C. Hersam at the Bat Sheva Seminar on Electron Transport in Molecular Junctions, Mizpe Hayamim, Israel (9/18/05).

[26] M. C. Hersam, "Observing and manipulating single molecule motion using scanning tunneling microscopy," presented orally by M. C. Hersam at the 230th American Chemical Society National Meeting, Washington, DC (8/29/05).

[27] M. C. Hersam, "Single molecule sensing, characterization, and actuation," presented orally by M. C. Hersam at the International Materials Research and Nanotechnology Workshop, Khon Kaen, Thailand (8/8/05).

[28] M. C. Hersam, "Probing silicon-based molecular electronics with scanning tunneling microscopy," presented orally by M. C. Hersam at the Molecular Conduction and Sensing Workshop, West Lafayette, Indiana (7/29/05).

[29] M. C. Hersam, "Characterizing charge transport in molecule-silicon junctions with scanning tunneling microscopy," presented as a poster by M. C. Hersam at the Gordon Research Conference on the Chemistry of Electronic Materials, New London, Connecticut (7/19/05).

[30] M. C. Hersam, "Introduction to nanoelectronics," presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, Washington, D.C. (7/14/05).

[31] N. P. Guisinger and M. C. Hersam, "Probing charge transport of isolated molecules bound to silicon using cryogenic ultrahigh vacuum scanning tunneling microscopy," presented orally by N. P. Guisinger at the 64th Physical Electronics Conference, Madison, Wisconsin (6/21/05).

[32] M. C. Hersam, "Probing silicon-based molecular electronics with scanning tunneling microscopy," presented orally by M. C. Hersam at the Columbia University Nanoscale Science and Engineering Center Seminar Series, New York, New York (4/27/05).

[33] M. C. Hersam, "Introduction to nanometer scale science and technology," presented orally by M. C. Hersam at the American Institute of Chemical Engineering Chicago Section Symposium, Chicago, Illinois (4/20/05).

[34] M. C. Hersam, "Probing electronic properties at the single molecule level on silicon surfaces," presented orally by M. C. Hersam at the Yale University Solid State and Optics Seminar Series, New Haven, Connecticut (4/13/05).

- [35] M. C. Hersam, "Probing charge transport through individual molecules on silicon surfaces," presented orally by M. C. Hersam at the American Physical Society March Meeting, Los Angeles, California (3/21/05).
- [36] M. C. Hersam, "Atomically precise fabrication and characterization of organosilicon nanostructures," presented orally by M. C. Hersam at the International Symposium on Frontier in Materials Design, Synthesis, and Measurements, Awaji, Japan (3/13/05).
- [37] M. C. Hersam, "Nanopatterning soft materials on silicon surfaces down to the single molecule level," presented orally by M. C. Hersam at the NSF/MEXT US-Japan Young Scientists Symposium on Bionanotechnology, Chicago, Illinois (3/8/05).
- [38] M. C. Hersam, "Characterization and manipulation of single molecules on surfaces with scanning probe microscopy," presented orally by M. C. Hersam at the Bioinspired Nanoscience and Molecular Machines PASI Workshop, Bariloche, Argentina (3/1/05).
- [39] M. C. Hersam, "Introduction to scanning probe microscopy," presented orally by M. C. Hersam at the Bioinspired Nanoscience and Molecular Machines PASI Workshop, Bariloche, Argentina (3/1/05).
- [40] R. Basu, J. D. Tovar, and M. C. Hersam, "Atomically precise fabrication and characterization of heteromolecular organosilicon nanostructures: Implications for silicon-based molecular electronics," presented as a poster by R. Basu at the Molecular-Scale Electronics VII Conference, San Diego, California (1/25/05).
- [41] N. L. Yoder, N. P. Guisinger, and M. C. Hersam, "Variable temperature charge transport measurements of molecule-silicon junctions using ultra-high vacuum scanning tunneling microscopy," presented orally by N. L. Yoder at the Molecular-Scale Electronics VII Conference, San Diego, California (1/25/05).
- [42] M. C. Hersam, "Molecular structures on silicon surface," presented orally by M. C. Hersam at the 32nd Conference on the Physics and Chemistry of Semiconductor Interfaces, Bozeman, Montana (1/25/05).
- [43] M. C. Hersam, "Single molecule sensing, characterization, and actuation," presented as a poster by M. C. Hersam at the National Academies Keck Future Initiatives Designing Nanostructures Conference, Irvine, California (11/20/04).
- [44] N. P. Guisinger, R. Basu, M. E. Greene, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance through molecular monolayers adsorbed to silicon surfaces with ultra-high vacuum scanning tunneling microscopy," presented orally by N. P. Guisinger at the 51st AVS International Symposium, Anaheim, California (11/18/04).
- [45] M. C. Hersam, "Nanoscale surface characterization and patterning strategies for organic and biological molecules," presented orally by M. C. Hersam at the Children's Memorial Research Center Colloquium, Chicago, Illinois (11/12/04).
- [46] M. C. Hersam, "Probing molecular conduction with scanning probe microscopy," presented orally by M. C. Hersam at the 2nd Workshop on Molecular Conduction, Evanston, Illinois (7/8/04).
- [47] M. C. Hersam, "Introduction to nanoelectronics," presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, Evanston, Illinois (6/30/04).
- [48] R. Basu, N. P. Guisinger, M. E. Greene, and M. C. Hersam, "Multi-step feedback controlled lithography: A processing technique for fabricating atomically registered organosilicon heterostructures using room temperature ultra-high vacuum scanning tunneling microscopy," presented orally by R. Basu at the 2004 TMS Electronic Materials Conference, Notre Dame, Indiana (6/23/04).
- [49] M. C. Hersam, "Characterization of silicon-based molecular resonant tunneling diodes with scanning tunneling microscopy," presented orally by M. C. Hersam at the TMS Joint Device Research Conference and Electronic Materials Conference Invited Session on Molecular Electronics and Carbon Nanotubes, Notre Dame, Indiana (6/23/04).
- [50] N. P. Guisinger, R. Basu, M. E. Greene, A. S. Baluch, and M. C. Hersam, "Room temperature negative differential resistance measured through molecular monolayers adsorbed to silicon surfaces with ultra-high vacuum scanning tunneling microscopy," presented orally by N. P. Guisinger at the American Vacuum Society Prairie Chapter 2004 Meeting, Urbana, Illinois (6/14/04).
- [51] N. L. Yoder, E. T. Foley, N. P. Guisinger, and M. C. Hersam, "A cryogenic variable temperature ultra-high vacuum scanning

tunneling microscope optimized for nanofabrication and characterization of individual molecules on silicon surfaces,” presented orally by N. L. Yoder at the American Vacuum Society Prairie Chapter 2004 Meeting, Urbana, Illinois (6/14/04).

[52] M. C. Hersam, “Resonant tunneling through individual molecules on silicon: Implications for electronics and chemical spectroscopy,” presented orally by M. C. Hersam at the Argonne National Laboratory Materials Science Division Colloquium, Argonne, Illinois (5/20/04).

[53] M. C. Hersam, “Nanoscale electrical and optical functionality in individual organic molecules and encapsulated single-walled carbon nanotubes,” presented orally by M. C. Hersam at the Molecular and Electronic Nanostructures Seminar Series, Urbana, Illinois (4/21/04).

[54] M. C. Hersam, “Single molecule electronics on silicon,” presented orally by M. C. Hersam at the 2004 Materials Research Society Spring Meeting, San Francisco, California (4/14/04).

[55] M. C. Hersam, “Silicon-based molecular electronics,” presented orally by M. C. Hersam at the Nanoengineering Domain Dinner, Evanston, Illinois (3/18/04).

[56] M. C. Hersam, “Probing charge transport through individual molecules on degenerately doped silicon surfaces,” presented orally by M. C. Hersam at the 34th Winter Colloquium on the Physics of Quantum Electronics, Snowbird, Utah (1/6/04).

[57] M. C. Hersam, “Probing charge transport through individual molecules on degenerately doped silicon surfaces,” presented orally by M. C. Hersam at the 34th Winter Colloquium on the Physics of Quantum Electronics, Snowbird, Utah (1/6/04).

[58] M. C. Hersam, “Nanoscale electrical and optical functionality in individual organic molecules and carbon nanotubes,” presented orally by M. C. Hersam at the France-USA Workshop on Molecular-Scale Electronics, Paris, France (12/18/03).

[59] M. C. Hersam, “Silicon-based molecular electronics,” presented orally by M. C. Hersam at the 15th Annual Beckman Frontiers of Science Symposium, National Academy of Sciences, Irvine, California (11/8/03).

[60] R. Basu, N. P. Guisinger, and M. C. Hersam, “Templated growth of one-dimensional molecular wires on Si(100) using multi-step feedback controlled lithography,” presented orally by R. Basu at the 2003 AVS International Symposium, Baltimore, Maryland (11/5/03).

[61] N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, “Observation of negative differential resistance measured through individual molecules on silicon at room temperature,” presented orally by N. P. Guisinger at the 2003 AVS International Symposium, Baltimore, Maryland (11/5/03).

[62] N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, “Room temperature negative differential resistance measured through individual molecules on silicon,” presented orally by M. C. Hersam at the Third IEEE Conference on Nanotechnology, San Francisco, California (8/12/03).

[63] M. C. Hersam, “Probing charge transport through molecule-semiconductor junctions with scanning tunneling microscopy,” presented orally by M. C. Hersam at the 2003 Workshop on Molecular Conduction, West Lafayette, Indiana (7/10/03).

[64] M. C. Hersam, “Introduction to nanoelectronics,” presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, Evanston, Illinois (7/9/03).

[65] M. C. Hersam, “Nanofabrication and characterization of electronic, photonic, and sensing devices down to the single molecule level,” presented orally by M. C. Hersam at the SPIE Photonics West Meeting, San Jose, California (1/29/03).

[66] N. P. Guisinger, R. Basu, E. T. Foley, and M. C. Hersam, “Direct charge transport measurements of individual organic molecules on semiconductor surfaces using scanning tunneling microscopy and spectroscopy,” presented orally by M. C. Hersam at the United Engineering Foundation Conference on Molecular-Scale Electronics, Key West, Florida (12/17/02).

[67] M. C. Hersam, “Nanoscale control of friction and chemistry on silicon surfaces,” presented orally by M. C. Hersam at the Materials Research Society Fall Meeting, Boston, Massachusetts (12/5/02).

[68] M. C. Hersam, “Materials science and engineering at the single molecule level,” presented orally by M. C. Hersam at the American Society of Mechanical Engineers International Mechanical Engineering Congress, New Orleans, Louisiana (11/19/02).

- [69] M. C. Hersam, "Molecular scale electromechanical systems," presented orally by M. C. Hersam at the Army Research Office Nanoelectromechanical Systems Workshop, Chicago, Illinois (11/14/02).
- [70] M. C. Hersam, "Nanoscale materials science and engineering down to the single molecule level," presented orally by M. C. Hersam at the Pennsylvania State University Materials Science and Engineering Colloquium, University Park, Pennsylvania (10/31/02).
- [71] N. P. Guisinger, R. Basu, and M. C. Hersam, "Atomic-level characterization and control of free radical surface chemistry using scanning tunneling microscopy," presented orally by N. P. Guisinger at the American Vacuum Society Prairie Chapter 2002 Meeting, Chicago, Illinois (10/7/02).
- [72] N. P. Guisinger, R. Basu, and M. C. Hersam, "Atomic level characterization and control of organosilicon surface chemistry using scanning tunneling microscopy," presented as a poster by N. P. Guisinger at the Center for Catalysis and Surface Science Annual Meeting, Evanston, Illinois (9/10/02).
- [73] M. C. Hersam, "Single molecule sensing, characterization, and actuation," presented orally by M. C. Hersam at the Symposium on Molecular Scale Devices, 6th World Multiconference on Systemics, Cybernetics, and Informatics, Orlando, Florida (7/18/02).
- [74] M. C. Hersam, "Nanofabrication and characterization of electronic, photonic, and sensing devices down to the single molecule level," presented orally by M. C. Hersam at the Michigan State University Electrical and Computer Engineering Colloquium, East Lansing, Michigan (3/28/02).
- [75] M. C. Hersam, "Nanoscale science and engineering education outreach programs," presented as poster by M. C. Hersam at the 3rd EC/NSF Workshop on Nanotechnology, Lecce, Italy (1/31/02 – 2/1/02).
- [76] M. C. Hersam, "Atomic-scale nanoelectronics," presented orally by M. C. Hersam at the University of Illinois at Chicago Electrical and Computer Engineering Department Colloquium, Chicago, Illinois (11/29/01).
- [77] M. C. Hersam, "Atomic-scale nanoelectronics," presented orally by M. C. Hersam at the IEEE Electron Devices/Circuits and Systems/Solid State Circuits Chicago Chapter Meeting, Motorola Center, Schaumburg, Illinois (10/25/01).
- [78] M. C. Hersam, "Single molecule engineering," presented as a poster by M. C. Hersam at the Argonne National Laboratory Center for Nanoscale Materials Workshop, Argonne, Illinois (10/22/01).
- [79]"Dielectric response of chloromethylsilyl dipolar rotors," Robert D. Horansky, Laura I. Clarke, Dominik Horinek, Gregg S. Kottas, Natalia Varaksa, Thomas F. Magnera, Tanja P. Hinderer, Josef Michl, and John C. Price, Trends in Nanotechnology 2002, Santiago de Compostella, Spain, Sept. 913, 2002 (poster).
- [80]"Dielectric relaxation of surface mounted molecular dipolar rotors," Gordon Research Conference Nanostructure Fabrication, August 2002, Tilton School, Tilton, NH (poster) [Laura Clarke*, Dominik Horinek, Tanja Hinderer*, Gregg Kottas, Natalia Varaksa, Thomas Magnera, Rob Horansky*, Josef Michl, John Price*, Daniel Kitayama*, M. Jon Dadras*, and Tim Black* Departments of *Physics and Chemistry and Biochemistry University of Colorado, Boulder, CO 80309]
- [81]"Dielectric response of chloromethylsilyl dipolar rotors on fused silica surfaces," 1st International Conference on Nanoscale/Molecular Mechanics, May 2002, Maui, HI (poster) [Laura Clarke*, Gregg Kottas, Tanja Hinderer*, Natalia Varaksa, Thomas Magnera, Rob Horansky*, Dominik Horinek, Josef Michl, John Price* University of Colorado at Boulder Departments of *Physics and Chemistry and Biochemistry]
- [82]"Dielectric response of chloromethylsilyl dipolar rotors on fused silica surfaces," Daniel Kitayama, Colorado-Wyoming Junior Academy of Sciences , April 27, 2002.
- [83]"Dielectric Relaxation of Dipolar Molecular Rotors," R.G. Herb Materials Physics Seminar, February 2003, University of Wisconsin, Madison, WI. [Laura Clarke]
- [84]"Dipolar Molecular Rotors," Special Colloquium, January 2003, North Carolina State University, Raleigh, NC. [Laura Clarke]

[85] Robert D. Horansky, Laura I. Clarke, Jose Nunez, Josef Michl , Miguel Garcia-Garibay, and John C. Price, "Dielectric Response of Molecular Dipolar Rotors on Insulating Surfaces," Salamanca, Spain. Trends in Nanotechnology Conference. September 5-9, 2003

[86] Laura I. Clarke, Mary Beth Mulcahy, Robert Horansky, Dominik Horinek, Xaiolai Zheng, Thomas Magnera, Josef Michl and John Price, "Dielectric Spectroscopy of Altitudinal Dipolar Molecular Rotors," Poster presentation at MRS Fall meeting, December 2003, Boston, MA.

[87] 2004 March Meeting of the American Physical Society, March 22-26, Palais des Congres de Montreal Montreal, Quebec, Canada "Dielectric Relaxation of 3D Dipolar Rotor Arrays", Robert D. Horansky, Laura I. Clarke, Tinh-Alfredo V. Khuong, Peter D. Jarowski, Miguel A. Garcia-Garibay, and John C. Price

[88] 2004 March Meeting of the American Physical Society, March 22-26, Palais des Congres de Montreal Montreal, Quebec, Canada "Dielectric Relaxation of Altitudinal Dipolar Molecular Rotors", L. I. Clarke, M. E. Mulcahy, R. D. Horansky, D. Horinek, X. Zheng, T. F. Magnera, J. Michl, J. C. Price

[89]"Rotor-Rotor Interactions in a Three Dimensional Lattice of Dipolar Molecular Rotors," Robert D. Horansky, Laura I. Clarke, Erick Winston, Jose Nunez, Miguel A. Garcia-Garibay, and John C. Price, 2005 March Meeting of the American Physical Society, March 21-25, Los Angeles.

[90]"Roto-electrics: Phenylene Molecular Rotor Crystals," John Price, PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina, Feb. 28-March 11, 2005.

[91]"Electronics for Nanotechnology Research," John Price, PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina, Feb. 28-March 11, 2005.

[92]"Roto-Electrics: Arrays of Interacting Polar Molecular Rotors," John C. Price, Robert Horansky, Erick Winston, Jason Underwood, Matthew Myers, ICCOSS XVII, Los Angeles, July 24-29, 2005.

[93]"Roto-Electrics: Arrays of Interacting Polar Molecular Rotors," John C. Price, Robert Horansky, Erick Winston, Jason Underwood, Matthew Myers, 230th ACS National Meeting, Washington, D.C., Aug. 28-Sept. 1, 2005.

[94]"Dynamics of polar guest molecules contained in cryptophane molecular crystals," Erick B. Winston, Robert D. Horansky, Matthew S. Myers, Jaroslav Vacek, and John C. Price, 2006 meeting of the American Physical Society, March 13-17, Baltimore, MD.

[95] "Nano-electromechanical structures for single molecule transport students and position sensing" Shawn Tanner and Charles Rogers, March 13, 2006, APS March Meeting, Baltimore MD.

[96]"Investigating mixtures of rotor molecules and liquid crystals by dielectric spectroscopy and optical microscopy", Debra Krause, Charles T. Rogers, Jose E. Nunez, and Miguel Garcia-Garibay, March 16, 2006, APS March Meeting, Baltimore MD.

[97]"Investigation of surface mounted molecular rotors through optical second harmonic generation", James D. Walker, Charles T. Rogers, Gregg S. Kottas, and Josef Michl, March 14, 2006, APS March Meeting, Baltimore MD.

[98]"Surface linear and nonlinear optical studies of dipolar rotor molecules", James D. Walker,

[99] Debra Krause, Gregg S. Kottas, Josef Michl, and Charles T. Rogers, August 26, 2005, American Chemical Society Meeting, Washington, DC.

[100] J. Michl, NSF Workshop "Emerging Opportunities of Nanoscience to Energy Conversion and Storage", Arlington, Virginia (11/21/05).

[101] J. Michl, Pacificchem 2005, Honolulu, Hawaii [Pacificchem 2005 Honolulu, Hawaii: invited lecture "Design and Characterization of Nanomaterials and Nanodevices" (12/15/05)].

[102] J. Michl, invited lecture, Gordon Conference on Electrochemistry, Santa Ynez Valley Marriott, Buellton, CA (2/12/06).

- [103] J. Michl, invited lecture, “Nanobio” symposium, APS Meeting, Baltimore, Maryland (3/13/05).
- [104] J. Michl, invited lecture, Kipping Award Symposium, ACS National Meeting, Atlanta (3/26/06).
- [105] Ratner, M. “Nano 201”, presented orally by M. Ratner at Columbia Univ., New York (2/2005).
- [106] Michl, J. “Artificial Surface-Mounted Molecular Rotors”, presented orally by J. Michl at a seminar at the University of Georgia, Athens, Georgia, (2/8/05).
- [107] Ratner, M. “Molecular nanofabrication: Arrays and Methods”, presented orally by M. Ratner at the 229th ACS meeting, San Diego, California (3/2005).
- [108] Ratner, M. “Molecular Dynamics of Rotor Arrays - Signals and Switches” presented orally by M. Ratner at the Bioinspired Nanoscience and Molecular Machines PASI Workshop, Bariloche, Argentina (3/1/05).
- [109] Casher, D. L.; Magnera, T. F.; Kottas, G. S.; Kobr, L.; Michl, J. “Detection and Characterization of Azimuthal Molecular Rotor Monolayers on SiO₂ Surfaces”, poster presentation by D. L. Casher at the PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina (3/8/05).
- [110] Mulcahy, M. E.; Zheng, X.; Magnera, T. F.; Bastl, Z.; Michl, J. “Characterization and Physical Measurements of Molecular Sized Rotors on Gold and Glass Surfaces”, poster presentation by M. E. Mulcahy at the PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina (3/8/05).
- [111] Michl, J; Caskey, D. C.; Kottas, G. S.; Varaksa, N.; Magnera, T. F.; Zheng, Z.; Galeotti, F.; Wang, B.; Bartl, Z. “Artificial Surface-Mounted Molecular Rotors”, presented orally by J. Michl at the PASI Workshop, Bariloche, Argentina, (3/8/05).
- [112] Magnera, T. F.; Vacek, J.; Michl, J. “Can Surface-Mounted Altitudinal Molecular Rotors Actually Rotate?”, presented orally by J. Vacek at the PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina (3/8/05).
- [113] Vacek, J.; Horinek, D.; Michl, J. “Computer Simulation of Surface-Mounted Molecular Rotors”, presented orally by J. Michl the PASI Bioinspired Nanoscience and Molecular Machines, San Carlos de Bariloche, Argentina (3/10/05).
- [114] Ratner, M. “Molecular nanofabrication: Arrays and Methods”, presented orally by M. Ratner as a Lowdin lecture, Univ. of Florida, Gainesville (4/2005).
- [115] Michl, J. “Artificial Surface-Mounted Molecular Rotors”, presented orally by J. Michl as the John Stauffer lecturer, University of Southern California, Los Angeles, California, (4/6/05).
- [116] Michl, J. “Artificial Surface-Mounted Molecular Rotors”, presented orally by J. Michl at a colloquium, Free University, Berlin, Germany, (4/19/05).
- [117] Vacek, J.; Kobr, L.; Miller, J.; Michl, J. “Design of Fast Artificial Light-Absorption Driven Molecular Rotor”, presented orally by J. Vacek at the 2nd Annual Conference on Foundations of Nanoscience, Snowbird, Utah, (4/27/2005).
- [118] Vacek, J.; Horinek, D.; Michl, J. “Molecular Dynamics of a Fast Artificial Electric-Field Driven Surface-Mounted Molecular Rotor: A Single-Molecule Parametric Oscillator”, poster presentation by J. Vacek at the 2nd Annual Conference on Foundations of Nanoscience, Snowbird, Utah, (4/27/2005).
- [119] Ratner, M. “Nano 201”, presented orally by M. Ratner at the European Materials Society, Strasbourg (5/2005).
- [120] Vacek, J.; Kobr, L.; Miller, J.; Michl, J. “Design of Fast Artificial Light-Absorption Driven Molecular Rotor”, presented orally by Jaroslav Vacek at the CERC III Younger Chemist Meeting, Baden Baden, Germany (05/04/2005).
- [121] Mulcahy, M. E.; Casher, D. L.; Magnera, T. F.; Kottas, G. S.; Kobr, L.; Zheng, X.; Clarke, L.; Michl, J. “Towards Freely Rotating Molecular Rotors on SiO₂”, poster presentation by M. E. Mulcahy and D. L. Casher, 38th Silicon Symposium, Boulder, Colorado,

(6/4/05).

- [122] Michl, J. "Physics of artificial molecular rotors", presented orally by J. Michl at the Nobel Symposium "Controlled Nanoscale Motion in Artificial and Biological Systems", Bäckaskog, Sweden, (6/14/05).
- [123] Mulcahy, M. E.; Casher, D. L.; Magnera, T. F.; Kobr, L.; Caskey, D. C.; Zheng, X.; Horinek, D.; Michl, J. "Artificial Surface-Mounted Molecular Rotors", presented orally by J. Michl at the ICCOSS XVII, Los Angeles, California, (7/28/05).
- [124] Magnera, T. F.; Casher, D. L.; Mulcahy, M. E.; Zheng, X.; Michl, J. "Detection of Rotary Motion in Surface-Mounted Dipolar Molecular Altitudinal Rotors", presented orally by T. Magnera at the 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [125] Michl, J. "Surface-Mounted Artificial Molecular Rotors: An Overview", presented orally by J. Michl at the 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [126] Vacek, J.; Horinek, D.; Prokop, A.; Michl, J. "Computer Simulations of Fluid Driven Molecular Rotors", presented orally by J. Vacek at the 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [127] Ratner, M. "Molecular Dynamics of Rotor Arrays - Signals and Switches" presented orally by M. Ratner at the 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [128] Casher, D. L.; Magnera, T. F.; Kottas, G. S.; Kobr, L.; Michl, J. "Detection and Characterization of Azimuthal Molecular Rotor Monolayers on SiO₂", poster presentation by D. L. Casher, 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [129] Caskey, D. C.; Michl, J. "Self-Assembled Prismatic Altitudinal Rotors", poster presentation by D. C. Caskey, 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [130] Kobr, L.; Michl, J. "Progress toward the Synthesis of a Third-Generation Altitudinal Molecular Rotor", poster presentation by L. Kobr, 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05).
- [131] Mulcahy, M. E.; Zheng, X.; Magnera, T. F.; Bastl, Z.; Michl, J. "Characterization of Altitudinal Molecular Rotors on Gold Surface", poster presentation by M. E. Mulcahy, 230th ACS National Meeting, Molecular Rotors Symposium, (8/28/05)
- [132] L. I. Clarke, M. E. Mulcahy, R. D. Horansky, D. Horinek, X. Zheng, T. F. Magnera, J. Michl, J. C. Price, "Dielectric Relaxation of Altitudinal Dipolar Molecular Rotors", 2004 March Meeting of the American Physical Society, Palais des Congres de Montreal Montreal, Quebec, Canada (3/22/04 - 3/26/04).
- [133] R. D. Horansky, L. I. Clarke, T.-A. V. Khuong, P. D. Jarowski, M. A. Garcia-Garibay, J. C. Price, "Dielectric Relaxation of 3D Dipolar Rotor Arrays", 2004 March Meeting of the American Physical Society, Palais des Congres de Montreal Montreal, Quebec, Canada (3/22/04 - 3/26/04).
- [134] D. C. Caskey, J. Michl, "Self-Assembly of Altitudinal Molecular Rotors for Surface Mounting", presented orally by J. Michl at the 227th ACS National Meeting, Anaheim, California (3/28/04 - 4/1/04).
- [135] T. F. Magnera, J. Michl, "Differential Barrier Height Imaging for the Detection of Surface-Mounted Dipolar Altitudinal Molecular Rotors", presented orally by J. Michl at the 227th ACS National Meeting Anaheim, California (3/28/04 - 4/1/04).
- [136] X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera, and J. Michl, "Dipolar and Non-Polar Altitudinal Molecular Rotors Mounted on an Au(111) Surface", presented orally by J. Michl at the 227th ACS National Meeting, Anaheim, California (3/28/04 - 4/1/04).
- [137] J. Michl, "Artificial Surface-Mounted Molecular Rotors", presented orally by J. Michl at the Foundations of Nanoscience, Snowbird, Utah (4/21/04 - 4/23/04).
- [138] X. Zheng, M. E. Mulcahy, D. Horinek, D. C. Caskey, R. D. Horansky, F. Galeotti, T. F. Magnera, L. I. Clarke, J. C. Price, N. Varaksa, L. Pospíšil, J. Michl, "Artificial Surface-Mounted Molecular Rotors", presented orally by J. Michl at an Organic Chemistry

Conference, Pardubice, Czech Republic (6/14/04 - 6/17/04).

- [139] D. Horinek, J. Michl, "Modeling a Surface-Mounted Molecular Parametric Oscillator", presented orally by J. Michl at the IAQMS Meeting, Menton, France (7/3/04 - 7/4/04).
- [140] D. Horinek, D. L. Casher, L. Kобр, T. F. Magnera, D. C. Caskey, and J. Michl, "Can fluid flow be used to drive surface-mounted altitudinal rotors?", presented orally by J. Michl at the 228th ACS National Meeting, Philadelphia, Pennsylvania (8/22/04 - 8/26/04).
- [141] Michl, J. "Artificial Surface-Mounted Molecular Rotors," presented orally by J. Michl at the France-USA Workshop on Molecular-Scale Electronics, Paris, France (December 18, 2003).
- [142] Ratner, M. A. "Molecular Junctions - Simple Transport and a Bit Beyond," presented orally by M. A. Ratner at the France-USA Workshop on Molecular-Scale Electronics, Paris, France (December 18, 2003).
- [143] Clarke, L. I.; Mulcahy, M. E.; Horansky, R.; Horinek, D.; Zheng, X.; Magnera, T. F.; Michl, J.; Price, J. C. "Dielectric Spectroscopy of Altitudinal Dipolar Molecular Rotors," poster presentation at MRS Fall meeting, Boston, MA (December 1 - 5, 2003).
- [144] Horansky, R. D.; Clarke, L. I.; Nunez, J.; Michl, J.; Garcia-Garibay, M.; Price, J. C. "Dielectric Response of Molecular Dipolar Rotors on Insulating Surfaces," presented orally by Rob Horansky at the Trends in Nanotechnology Conference, Salamanca, Spain (September 5-9, 2003).
- [145] Michl, J. "Unusual Molecules: Artificial Surface-Mounted Altitudinal Rotors," presented orally by J. M. Michl at the International Symposium on Reactive Intermediates and Unusual Molecules, Reykjavik, Iceland (August 17 - 22, 2003).
- [146] Horinek, D.; Michl, J. "Molecular Dynamics of Surface-Mounted Azimuthal and Altitudinal Molecular Dipolar Rotors Driven by Electric Field or Fluid Flow," poster presented by J. Michl at the XIth ICQC, Bonn, Germany (July 19 - 26, 2003).
- [147] Kottas, G. S.; Gala, K.; Michl, J. "Electronic Spectra of Cyclobutadienecobaltcyclopentadienyl Sandwich Complexes: Experimental and TD DFT Results for Cobalt and Nickel," poster presented by J. M. Michl at the XIth ICQC, Bonn, Germany (July 19 - 26, 2003).
- [148] Rooklin, D.; Fogarty, H. A.; Schepers, T.; Michl, J. "Sigma Electron Delocalization in Oligosilanes: TD DFT Results for Electronic Excitation as a Function of Chain Length and Conformation," poster presented by J. Michl at the XIth ICQC, Bonn, Germany (July 19 - 26, 2003).
- [149] Kottas, G. S.; Michl, J. "Azimuthal Dipolar Rotors on Silica Surfaces: Dielectric Response of Simple Rotors and Synthetic Efforts Toward the Next Generation," poster presentation by G. S. Kottas at the Gordon Research Conference, Plymouth, New Hampshire (June 29 - July 4).
- [150] Kottas, G. S.; Michl, J. "Molecular Dipolar Rotors: Dielectric Response of Simple Rotors and Synthetic Efforts Toward the Next Generation," presented orally by G. S. Kottas at the Gordon Research Conference, Plymouth, New Hampshire (June 29 - July 4).
- [151] Michl, J. "Artificial Surface-Mounted Molecular Rotors: Theory and Experiment," presented orally by J. Michl at Jortnerfest, Tel Aviv, Israel (June 16 - 18, 2003).
- [152] Michl, J. "Artificial Surface-Mounted Molecular Rotors", presented orally by J. Michl at the Quilmes Nanoscience Workshop: Molecular Electronics and Quantum Dots (May 16 - 20, 2003).
- [153] Michl, J. "Artificial Surface-Mounted Molecular Rotors," presented orally by J. Michl at the CERC3 Young Chemists Workshop, Gothenburg, Germany (April 11 - 13, 2003).
- [154] Clarke, L.; Horansky, R.; Hinderer, T.; Price, J.; Nunez, J.; Khuong, T.; Garcia-Garibay, M.; Horinek, D.; Kottas, N.; Varaksa, T.; Magnera, T.; Michl, J. "Dielectric Relaxation of Molecular Dipolar Rotors," presented orally by Laura Clarke at the March Meeting 2003 of the American Physical Society, Austin, Texas (March 3 - 7, 2003).
- [155] Michl, J. "Artificial Surface-Mounted Molecular Dipolar Rotors," presented by J. Michl at the March Meeting 2003 of the American Physical Society, Austin, Texas (March 3 - 7, 2003).
- [156] Michl, J. "Surface-Mounted Artificial Molecular Motors," presented orally by J. Michl at RatnerFest (January 24 - 25, 2003).

Number of Presentations: 156.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

- [1] N. L. Yoder and M. C. Hersam, "Probing the performance and reliability of silicon-based molecular electronic devices with ultra-high vacuum scanning tunneling microscopy," Proceedings of the 3rd Annual Foundations of Nanoscience Conference, 1, 80 (2006).
- [2] N. P. Guisinger, R. Basu, M. E. Greene, A. S. Baluch, and M. C. Hersam, "Characterization of silicon-based molecular resonant tunneling diodes with scanning tunneling microscopy," Proceedings of the 62nd Device Research Conference (IEEE, New York, 2004), p. 195.
- [3] M. C. Hersam, "Single molecule sensing, characterization, and actuation," Proceedings of the 6th World Multiconference on Systemics, Cybernetics, and Informatics, 17, 338 (2002).
- [4] Vacek, J.; Horinek, D.; Michl, J. "Calculations of molecular rotors and motors", Proceedings of the HPCMP users group conference, 2005, IEEE, 1.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

4

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

(d) Manuscripts

- [1] J.J. de Jonge, M. A. Ratner, S. W. de Leeuw "Local Field Controlled Switching in a One-Dimensional Dipolar Array," J. Phys. Chem. B, accepted for publication.
- [2] Vacek, J.; Chocholoušová, J.; Kobr, L.; Miller, J.; Michl, J. "Calculations of Light-Absorption Driven Molecular Rotors", Proceedings of the HPCMP users group conference, 2006, IEEE, submitted for publication.
- [3] Horansky, R. D.; Magnera, T. F.; Price, J. C.; Michl, J. "Artificial Dipolar Molecular Rotors", in Controlled Nanoscale Motion in Biological and Artificial Systems, Linke, H.; Måansson, A., Eds., Berlin, Springer-Verlag, in press.
- [4] Vacek, J.; Michl, J. "Artificial Surface-Mounted Rotors: Molecular Dynamic Simulations" Adv. Functional Mater. accepted for publication.

Number of Manuscripts: 4.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Andrew S. Baluch	No
Norma E.S. Contes	No
Liam S.C. Pingree	No
Rajiv Basu	No
Mark E. Greene	No
Nathan L. Yoder	No
Charles W. Teplin	No
James Walker	No
Deborah Krause	No
Shawn Tanner	No
Jason Underwood	No
Erick Winston	No
Robert Horansky	No
Gregg Kottas	No
Lukas Kobr	No
Matthew Fete	No
Peter Schreiber	No
Deb Casher	No
John Miller	No

FTE Equivalent:

Total Number: 19

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Edward T. Foley	No
John D. Tovar	No
Laura Clarke	No
Li Cheng	No
Duska Popovic	No
Dominik Horinek	No
Francesco Galeotti	No
Wenjun Lu	No
Natalia Varaksa	No

FTE Equivalent:

Total Number: 9

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>	National Academy Member
Prof. John Price	No	
Prof. Charles Rogers	No	
Prof. Mark Hersam	No	

FTE Equivalent:

Total Number: 3

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Andrew S. Baluch	No
Shaun P. Elder	No
James S. Fakonas	No
Shengyao Li	No
Matthew J. Schmitz	No
Peter Lowell	No
Ed Thiemann	No
Tanja Hinderer	No
Tim Black	No
Jon Dadras	No
Drew Marcy	No
Zack Murray	No
Faith Jordan	No
Charles Hagerdorn	No
Elizabeth Baker,	No
Mathew Myers	No
Leah A. Edelman	No
William T. Gathright	No
Bill Bockrath	No
Navindra Gunawardena	No
Gabriel Drohen	No
Craig Manning	No

FTE Equivalent:

Total Number: 22

Names of Personnel receiving masters degrees

<u>NAME</u>	
Andrew S. Baluch	No
Total Number:	1

Names of personnel receiving PHDs

<u>NAME</u>	
Gregg Kottas	No
Mark E. Greene	No
Rajiv Basu	No
Robert D. Horansky	No
Mary Beth Mulcahy	No
Deb Casher	No
Erick Winston	No
Jason Underwood	No

Total Number: 8

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Dr. Thomas Magnera	No
Dr. Jaroslav Vacek	No
Dr. Jeroen de Jonge	No
Dr. Yuri Berlin	No
Dr. John Downing	No

FTE Equivalent:

Total Number: 5

Sub Contractors (DD882)

Inventions (DD882)

Project Objective

Most mechanical machines contain rotating parts and it is likely that the nanomachines of the future will be no exception. We proposed to find out how rotors 1-2 nm in size can be synthesized and attached to surfaces, and what their fundamental properties are. We studied their equilibrium behavior and driven response, the effects of rotational barriers and friction, and mutual and environmental interactions with potential future applications in mind in areas as diverse as molecular transistors, extremely compact microwave signal processing components, and micro-fluidic devices.

The projected involved the preparation, surface mounting, and characterization of single molecular rotors with both vertical and horizontal shafts, and both with and without large dipole moments. Our basic device is a surface mounted molecular dipolar rotor that has a base or bases that attach covalently to a flat insulating surface and support an axle oriented either perpendicularly to the surface by a single base, which in turn support a balanced 1–2 nm diameter rotor portion with a large in-plane electric dipole moment or support an axle oriented parallel to the surface by two bases and a similar rotor. The bearing consists of a single covalent bond, a fundamental element of molecular-scale mechanics.

Summary of Results

Hersam Contribution

Within the Molecular Rotors DURINT, the Hersam Research Group has focused on developing ultra-high vacuum (UHV) scanning tunneling microscopy (STM) techniques for characterizing and fabricating molecular rotor arrays on silicon surfaces. Included here is a summary of the major accomplishments over the five year duration of the DURINT:

(1) A variable temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) optimized for probing and manipulating individual molecules on silicon surfaces has been constructed and tested.

Figure MH1(a) contains a photograph of the variable temperature STM in a UHV chamber that achieves a base pressure of 10^{-11} Torr. The microscope is suspended on a spring suspension stage with magnetic eddy current damping for vibration isolation. The entire vibration isolation stage and microscope are contained within two gold plated copper thermal shields. The inner shield is in direct contact with the liquid helium cryostat and the outer shield is in direct contact with the boil off from the liquid helium. In addition, internal heaters are mounted on the roof plate of the thermal shrouds to enable variable temperature operation between the liquid helium base temperature and room temperature. Figure MH1(b) shows a representative image taken with the variable temperature UHV STM. Clear atomic resolution is observed on the Si(100)-2×1:H surface. In addition, the microscope is capable of atomic resolution feedback controlled lithography (FCL). The image in Figure 1(b) shows a 3 by 3 array of individual dangling bonds patterned with FCL. The design of this instrument has been documented in a *Review of Scientific Instruments* article (E. T. Foley, N. L. Yoder, N. P. Guisinger, and M. C. Hersam, “Cryogenic variable temperature ultra-high vacuum scanning tunneling microscope for single molecule studies on silicon surfaces,” *Rev. Sci. Instrum.*, **75**,

5280 (2004)) and a U.S. Patent application (“Cryogenic variable temperature scanning tunneling microscope,” E. T. Foley and M. C. Hersam, U.S. Patent application filed 11/30/05).

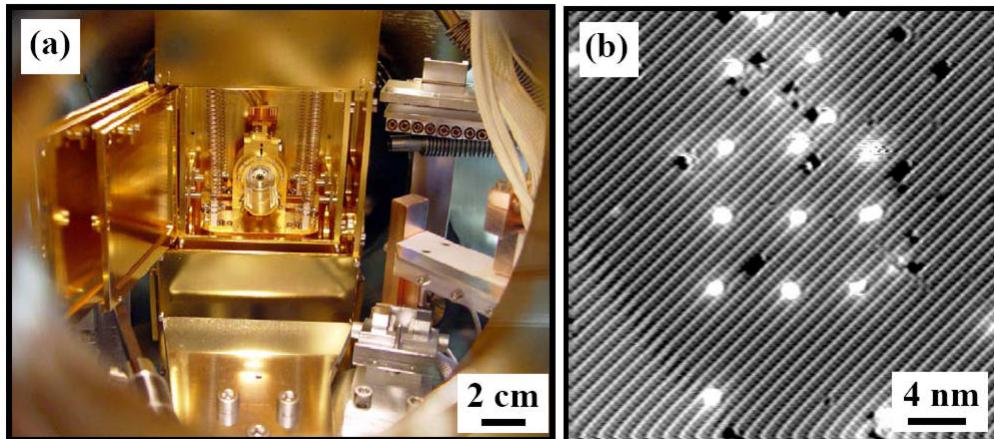


Figure MH1. (a) Photograph of the completed variable temperature STM as viewed through the UHV chamber view port. (b) An array of individual dangling bonds on the Si(100)-2×1:H surface following nanopatterning with feedback controlled lithography. This image demonstrates the atomic resolution imaging and patterning capability of the variable temperature UHV STM.

(2) Aza-norbornadiene rotors have been synthesized, mounted on silicon surfaces, and characterized with UHV STM.

Aza-norbornadiene analogs were studied as molecular rotors that can be mounted on Si(100) surfaces. In particular, n-trimethylsilyl-7-azanorbornadiene (TMSAN) was synthesized by the Michl Research Group at the University of Colorado and shipped to Northwestern University for UHV STM analysis. Figure MH2 shows a UHV STM image of a clean Si(100)-2×1 surface following exposure to a submonolayer coverage of TMSAN. The insets to Figure 2 illustrate that two distinct features were observed in the UHV STM images. One class of features appears confined to a single dimer row and has been identified as intra-row binding. The other class of features bridges two dimer rows and has been identified as inter-row binding. Figures MH3(a,b) schematically show the possible binding orientations of TMSAN on the Si(100)-2×1 surface. Since multiple binding orientations are possible for TMSAN, the orientation of the top rotating ligand could impact the construction of rotor arrays. Consequently, VASP calculations were performed in collaboration with Dr. Jeffrey Reimers of the University of Sydney to determine the orientation of the top ligand on the TMSAN molecule. These calculations showed that the axis of the rotating ligand was perpendicular to the surface as schematically shown in Figure 3(c). The cylindrical symmetry of this azimuthal rotor geometry minimizes the effect of multiple binding orientations and suggests that TMSAN or similar molecules are suitable for the construction of rotor arrays on silicon. Furthermore, due to cooperative motion of the methyl groups, the rotation barrier was calculated to be ~0.3 kcal/mol, which implies that the top ligand is in a free rotational state at room temperature. This relatively low rotational barrier suggests that multiple regimes of rotor behavior can be accessed via cryogenic variable temperature measurements.

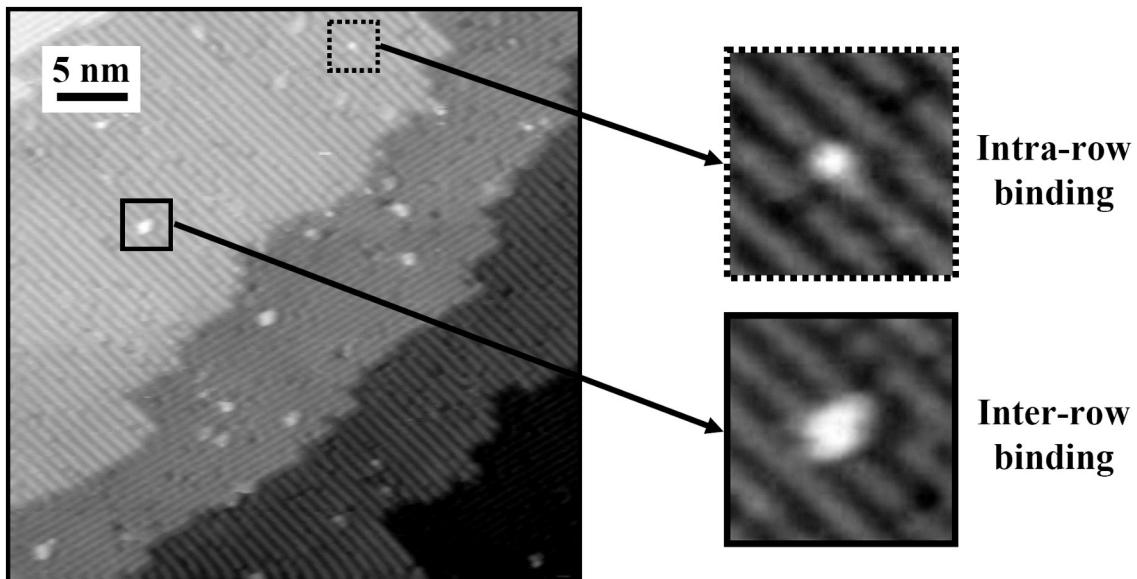


Figure MH2. UHV STM image of a submonolayer coverage of n-trimethylsilyl-7-azanorbornadiene on Si(100)-2×1. Two distinct binding conformations are observed as shown in the insets.

These experiments suggested that aza-norbornadiene analogs are suitable for dipolar rotor array studies. Consequently, it was critical to show that aza-norbornadiene analogs are compatible with UHV STM based nanofabrication techniques. Figure MH4 illustrates the general patterning strategy that was demonstrated for TMSAN. In particular, the chemically inert hydrogen passivated Si(100) surface was used as a starting substrate. By locally increasing the tip-sample bias, kinetically energetic electrons can stimulate desorption of hydrogen from the surface with atomic resolution. When the lithographically defined surface is exposed to molecules (e.g., TMSAN) in the gas phase, they react preferentially with the silicon dangling bonds. Following patterning, the properties of the molecules were then studied as a function of intermolecular spacing using STM topographic and spectroscopic imaging modes. These results were documented in a *Nanotechnology* paper that was co-authored by the Hersam, Michl, and Reimers Research Groups (B. Wang, X. Zheng, J. Michl, E. T. Foley, M. C. Hersam, A. Bilić, M. J. Crossley, J. R. Reimers, and N. S. Hush, “An azanorbornadiene anchor for molecular-level construction on silicon(100),” *Nanotechnology*, **15**, 324 (2004)).

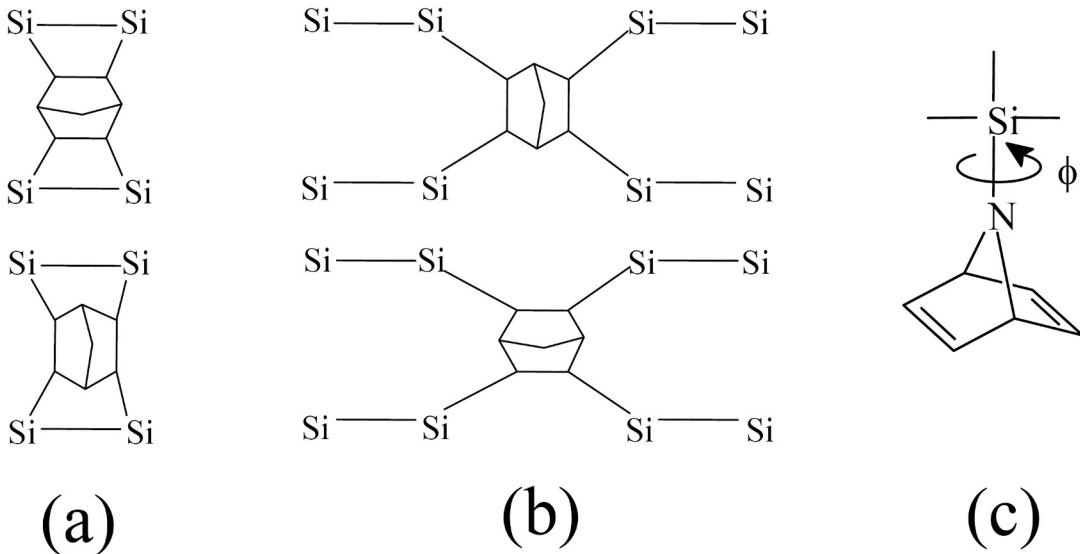


Figure MH3. Possible (a) intra-row and (b) inter-row binding conformations for aza-norbornadiene analogs. (c) Calculations indicate that n-trimethylsilyl-7-azanorbornadiene adopts an azimuthal rotor conformation.

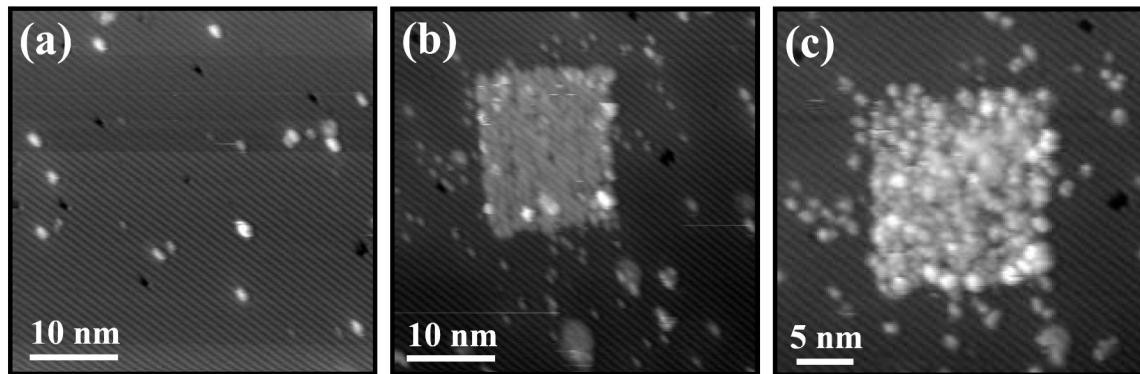


Figure MH4. (a) Hydrogen passivated Si(100) surface. (b) The same area following electron stimulated desorption of hydrogen from a 10 nm box. (c) n-trimethylsilyl-7-azanorbornadiene selectively reacts with the patterned square.

(3) Nitroxyl free radical chemistry has been used for patterning one-dimensional and two-dimensional molecular arrays on silicon with FCL.

In order for FCL to be effectively used for patterning arrays of surface-mounted molecular rotors, a molecular attachment chemistry needed to be developed that would react with individual silicon dangling bonds. Following a suggestion by Josef Michl, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was identified as a candidate molecule that would react with a single dangling bond to form a stable silicon-oxygen covalent bond. Figures MH5(a) and MH5(b) illustrate individual dangling bonds patterned with FCL on the Si(100)-2×1:H surface before and after gas phase TEMPO deposition in UHV. These images show that individual TEMPO molecules react with the patterned dangling bonds without damage to the surrounding hydrogen passivated surface. Figure MH5(c) further shows two one-dimensional arrays of TEMPO molecules patterned with FCL. These results illustrate that nitroxyl free radical binding

chemistry coupled with FCL is suitable for the formation of atomically precise one-dimensional and two-dimensional molecular rotor arrays on silicon. This work was documented in *Surface Science* (M. E. Greene, N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, “Nitroxyl free radical binding to Si(100): A combined STM and computational modeling study,” *Surface Science*, **559**, 16 (2004)). In addition, the TEMPO chemistry was utilized in a series of silicon-based molecular electronics papers from the Hersam Research Group, thus demonstrating the flexibility and impact of this novel surface chemistry: [1] R. Basu, N. P. Guisinger, M. E. Greene, and M. C. Hersam, *Appl. Phys. Lett.*, **85**, 2619 (2004); [2] A. S. Baluch, N. P. Guisinger, and M. C. Hersam, *TMS Lett.*, **1**, 125 (2004); [3] M. C. Hersam and R. G. Reifenberger, *MRS Bull.*, **29**, 385 (2004); [4] N. P. Guisinger, R. Basu, M. E. Greene, A. S. Baluch, and M. C. Hersam, *Nanotechnology*, **15**, S452 (2004); [5] N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, *Nano Letters*, **4**, 55 (2004); [6] N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam, *Ann. N. Y. Acad. Sci.*, **1006**, 227 (2003).

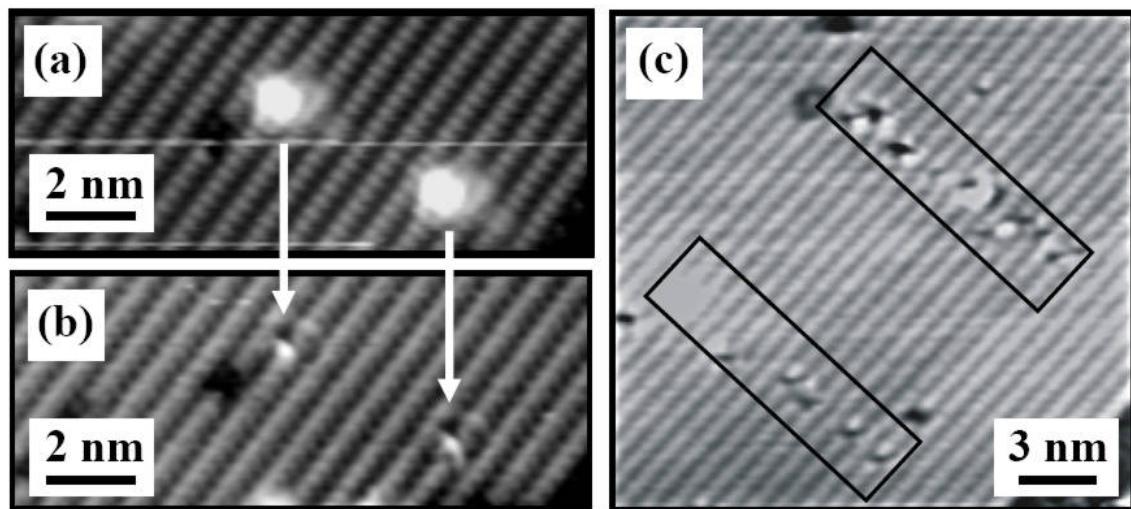


Figure MH5. (a) Two dangling bonds patterned with feedback controlled lithography on the Si(100)-2×1:H surface. (b) Individual TEMPO molecules selectively react with the pre-patterned dangling bonds. (c) Two one-dimensional arrays of TEMPO molecules following feedback controlled lithography on the Si(100)-2×1:H surface.

(4) The atomic level robustness of the Si(100)-2×1:H surface following liquid phase solvent treatments has been verified.

To date, atomically precise patterning with FCL has been limited to molecules that can be delivered to the Si(100)-2×1:H surface in the gas phase in UHV. However, many of the rotor molecules being synthesized by the Michl Research Group are limited to deposition via liquid phase solvent treatments. In order for these molecules to be tethered to FCL nanopatterns, the Si(100)-2×1:H surface must survive exposure to solvent treatments in an atmospheric pressure environment. Towards this end, a controlled atmosphere nitrogen glove box was directly interfaced to the UHV STM chamber. After taking appropriate measures to shield the sample surface during transit from UHV to the glove box, the Si(100)-2×1:H surface was shown to be unperturbed at the atomic scale following exposure to atmospheric pressure nitrogen. Furthermore, this work was extended by studying the atomic level quality of the hydrogen passivated Si(100) surface following exposure to a variety of solvents. The results are

summarized in Figure 6 where STM images are shown following treatments in dichloromethane, toluene, and water. In particular, Figures MH6(a) and MH6(b) show that the Si(100)-2×1:H surface sustains negligible damage even at the atomic scale following exposure to dichloromethane and toluene respectively. On the other hand, Figure MH6(c) shows that unsparged water causes significant perturbation of the surface. By minimizing dissolved oxygen, this perturbation was significantly reduced by sparging the water with nitrogen before surface exposure as seen in Figure MH6(d). Overall, a number of solvents have been identified that can be used for delivering molecular rotors to FCL patterned Si(100)-2×1:H surfaces. These results were documented in the *Journal of Vacuum Science and Technology* (A. S. Baluch, N. P. Guisinger, R. Basu, E. T. Foley, and M. C. Hersam, “Atomic-level robustness of the Si(100)-2×1:H surface following liquid phase chemical treatments in atmospheric pressure environments,” *J. Vac. Sci. Technol. A*, **22**, L1 (2004)).

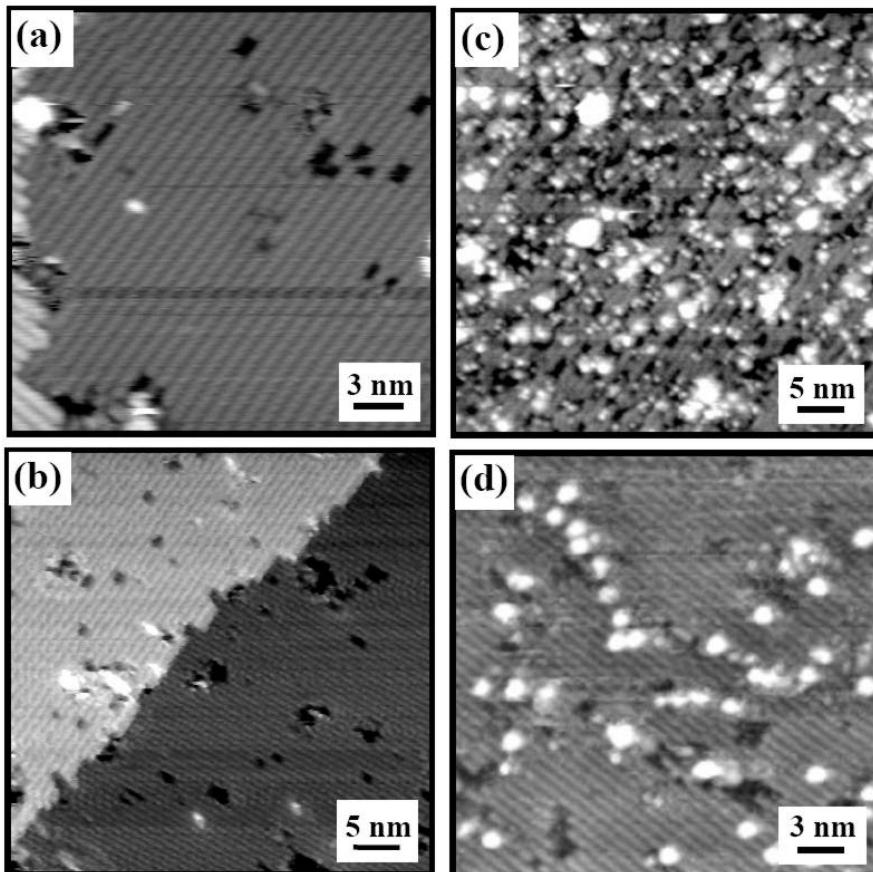


Figure MH6. UHV STM images of the Si(100)-2×1:H surface following exposure to a variety of solvents in an atmospheric pressure nitrogen glove box. (a) Dichloromethane. (b) Toluene. (c) Unsparged water. (d) Nitrogen sparged water.

(5) Molecular rotor behavior has been characterized for a series of styrene-like molecules on silicon surfaces using UHV STM.

UHV STM characterization has been accomplished for 4-methoxystyrene rotor molecules on the Si(100) surface. Figure MH7 schematically illustrates the expected [2 + 2] cycloaddition

binding configuration of a 4-methoxystyrene molecule to a silicon dimer and the corresponding STM image of a submonolayer coverage of 4-methoxystyrene on clean Si(100). Several of the molecules show intramolecular streaks parallel to the fast scan direction of the STM tip, thus suggesting the occurrence of a lateral displacement of a portion or the entire molecule. Due to the rotational degree of freedom of the methoxy group, a flip-flop switching behavior at room temperature is plausible and suggests that this intramolecular motion would lead to the observed streaks in the STM images. However, a closer inspection of the STM images reveals that the length scales of the lateral shifts are too large to be explained simply by the expected rotor-like behavior of the methoxy group on a fixed chemisorbed molecule. Since an STM image measures the spatial extent of the local electronic density of states rather than the position of the atomic nuclei, it is possible that a small displacement in the position of the methoxy group could give rise to a much larger lateral shift in the STM image even if the molecule remained anchored to its original adsorption site. However, additional STM images indicate direct evidence for translation of the entire molecule along the dimer row on the silicon surface. Consequently, the observed switching behavior for 4-methoxystyrene is likely explained by motion that includes breaking of carbon-silicon bonds between the molecule and the underlying substrate.

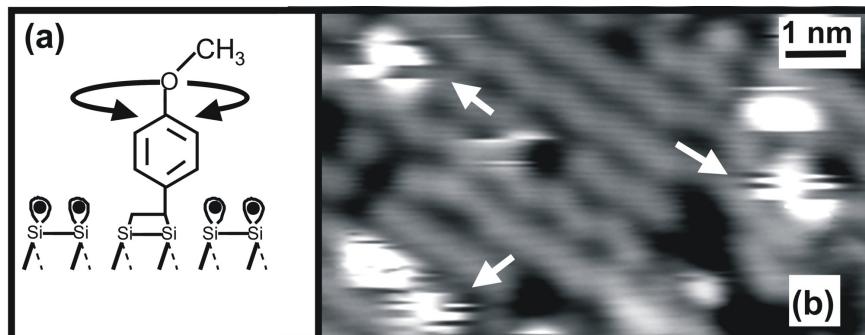


Figure MH7. (a) Schematic of [2+2] cycloaddition of a 4-methoxystyrene molecule on a dimer on the clean Si(100) surface. The methoxy group is expected to have the rotational degree of freedom indicated in the figure. (b) UHV STM image of 4-methoxystyrene molecules on the clean Si(100) surface following a dose of 0.7 L. Several of the molecules (indicated by white arrows) exhibit multiple switching events. Imaging conditions are sample bias of -2.0 V and tunneling current of 0.1 nA .

Figure MH8 schematically shows an alternative binding configuration where the 4-methoxystyrene molecule bridges two dimers along a dimer row on the Si(100) surface. Motion between this cross-dimer configuration and the single dimer configuration produces a lateral translation of the molecule that is consistent with the STM data. As shown schematically in Figure MH8(b), motion between these two configurations requires the breaking of one carbon-silicon covalent bond. This bond breaking is somewhat surprising since the chemisorption of vinyl groups to silicon dimers is typically stable at room temperature. Furthermore, while carbon-silicon bond breaking by the STM tip has been previously reported for aromatic organic molecules on Si(100), this mechanism is usually inefficient at the benign scanning conditions of -2 V and 0.1 nA . For example, Figure MH9 illustrates that UHV STM images of styrene molecules on clean Si(100) do not exhibit switching behavior under these scanning conditions. Consequently, 4-methoxystyrene appears to be especially susceptible to tip-induced molecular motion.

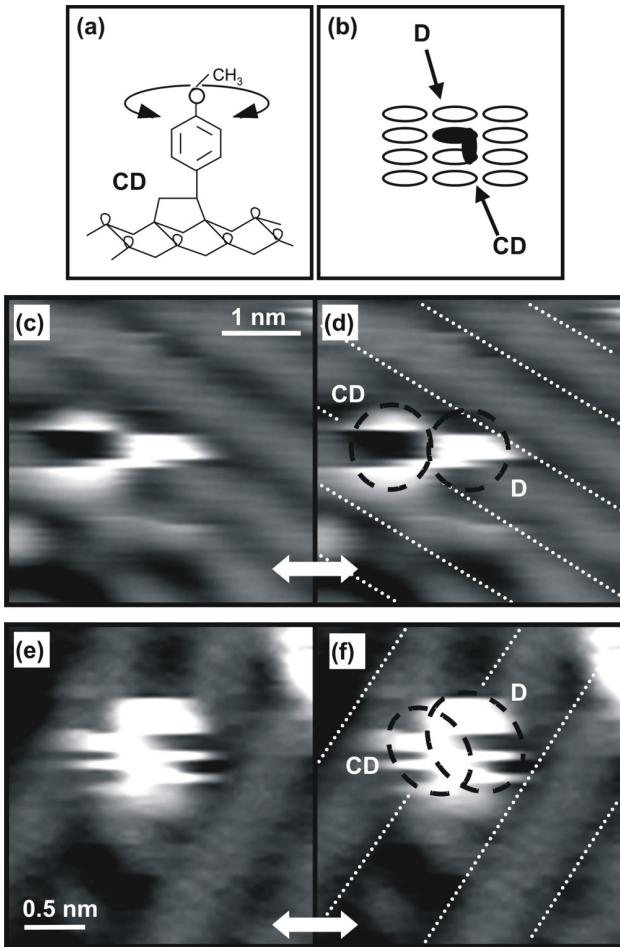


Figure MH8. (a) Schematic of a 4-methoxystyrene molecule chemisorbed in a cross-dimer (CD) configuration. (b) Schematic of a 4-methoxystyrene molecule alternately switching between a dimer (D) and a cross-dimer (CD) configuration. (c)–(f) Two pairs of UHV STM images showing a 4-methoxystyrene molecule switching between a dimer binding (indicated by ‘D’) and a cross-dimer binding configuration (indicated by ‘CD’). The white lines have been drawn to indicate the dimer rows and the black dotted circles indicate the spatial extent of the molecules in their bistable configurations. In both cases, the imaging conditions were sample bias of -2.0 V and tunneling current of 0.1 nA.

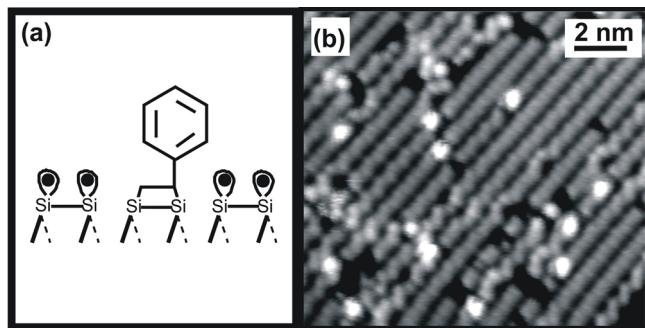


Figure MH9. (a) Schematic of chemisorption of a styrene molecule to a Si(100) dimer. (b) UHV STM image of styrene molecules on clean Si(100) following a dose of 0.2 L. In contrast to 4-methoxystyrene, no switching events are observed in this case. Imaging conditions are sample bias of -2.0 V and tunneling current of 0.1 nA.

Visual comparison of the structure of 4-methoxystyrene and styrene quickly reveals that these molecules are identical except for the presence of the methoxy group on 4-methoxystyrene. While this methoxy group may influence the detailed electronic structure of 4-methoxystyrene compared to styrene, it also represents a rotational degree of freedom that is not present in styrene. Therefore, we suspected that excitation of this rotary motion could couple to other vibrational modes in the molecule that would increase the likelihood of carbon-silicon bond breaking. To test this hypothesis, we sought a 4-methoxystyrene analog that removed the rotational degree of freedom of the methoxy group without introducing substantial changes to the electronic and chemical properties of the molecule. Following an established protocol, we synthesized 5-vinyl-2,3-dihydrobenzofuran, which is a molecule that eliminates the rotational degree of freedom by covalently linking the methoxy group back to the aromatic ring.

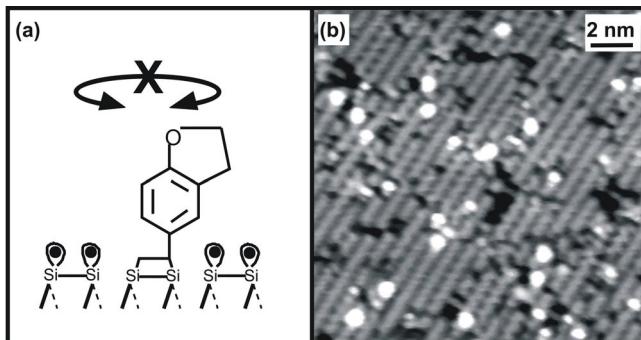


Figure MH10. (a) Schematic of a 5-vinyl-2,3-dihydrobenzofuran bound to Si(100). This molecule is analogous to 4-methoxystyrene except that its methoxy group is covalently linked to the aromatic ring in order to inhibit its rotational degree of freedom. (b) UHV STM image of a submonolayer coverage of 5-vinyl-2,3-dihydrobenzofuran on the clean Si(100) surface following a dose of 0.4 L. No switching events are observed in this case. Imaging conditions are sample bias of -2.0 V and tunneling current of 0.1 nA.

Figure MH10(a) shows a schematic depiction of 5-vinyl-2,3-dihydrobenzofuran bound to the Si(100) surface. The UHV STM image of Fig. MH10(b) confirms that this molecule does not experience the molecular motion observed for 4-methoxystyrene under identical scanning conditions. Interestingly, measurements on 2-methoxystyrene and 3-methoxystyrene also reveal no molecular motion at these experimental conditions. Thus, it appears that the intramolecular rotational degree of freedom provided by the methoxy group *and* the orientation of the rotor axis within 4-methoxystyrene enhances its likelihood of molecular motion. Overall, these results have been documented in the *Journal of Vacuum Science and Technology* (R. Basu, J. D. Tovar, and M. C. Hersam, “Scanning tunneling microscopy study of single molecule motion on the Si(100)- 2×1 surface,” *J. Vac. Sci. Technol. B*, **23**, 1785 (2005)).

(6) Technology Transfer to DURINT Collaborators at NIST

Following discussions with Mark Keller and Mark Dalberth of NIST at a DURINT team meeting, collaborative experiments were performed to demonstrate the feasibility of fabricating nanopatterned molecular rotor single electron transistors (SETs). The long term goal of this project is to use conductive atomic force microscope field induced oxidation as a strategy for nanopatterning molecular rotors in close proximity to the gate of a SET. As a first step towards this goal, the NIST collaborators supplied the Hersam Research Group with a silicon dioxide

substrate that is used in the fabrication of SETs. In order for the proposed device fabrication strategy to be successful, field induced oxidation needed to be demonstrated on the SET substrate. By using a conductive atomic force microscope contained within a controlled humidity glove box as shown in Figure MH11(a), field induced oxidation was successfully accomplished on the NIST substrate. Local oxidation was achieved at biases as low as 5 volts as illustrated in Figure MH11(b). In future experiments, a complete SET will be fabricated and coated with an inert trichlorosilane monolayer (e.g., octadecyltrichlorosilane). Field induced oxidation will then be used to locally form a freshly oxidized nanopattern near the gate of the SET. Molecular rotors will then be selectively deposited on the oxide nanopattern. The influence of the dipolar molecular rotation on the SET device characteristics will subsequently be studied. The dynamics of nanopatterning with atomic force microscopy have been documented in *Small* (M. C. Hersam, “Monitoring and analyzing nonlinear dynamics in atomic force microscopy,” *Small*, **2**, 1122 (2006)).

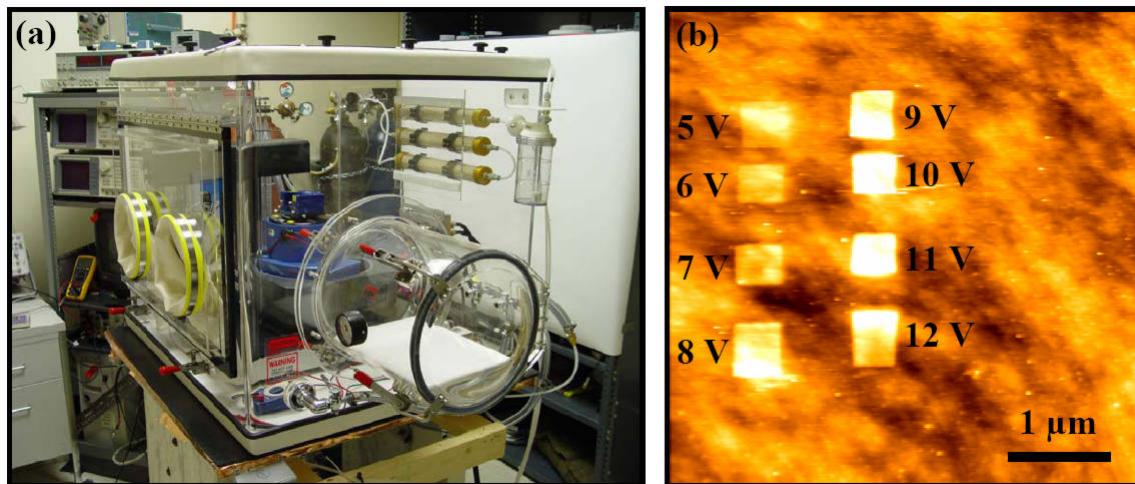


Figure MH11. (a) Conductive atomic force microscope enclosed in a controlled humidity glove box. This experimental apparatus is used for field induced oxidation nanopatterning. (b) Demonstration of field induced oxidation at a variety of biasing conditions on a silicon dioxide single electron transistor substrate supplied by Mark Keller and Mark Dalberth of NIST.

Price Contribution

Chloromethylsilyl Rotors on Quartz Glass (*Laura Clarke, Tanja Hinderer, Robert Horansky*)

We have used surface-sensitive dielectric spectroscopy to characterize a disordered 2-d array of chloromethylsilyl rotors on fused silica, Fig. JP1. The rotor molecules were covalently attached to the fused silica surface between co-planar interdigital electrodes, and the response to an in-plane electric field was observed by measuring the capacitance and loss tangent (dissipation factor) of the electrode pair.

In chloromethylsilyl the barrier height for rotation is much larger than the temperature, so we expect to see thermal hopping in an approximately three-fold symmetric rotational

potential. For a single barrier to rotation (each molecule having the same rotational potential with three identical wells), we would observe a single Debye relaxation peak in a plot of the loss tangent versus temperature, located at the temperature where the hopping frequency of the rotors equals the frequency of the applied field. The width of the peak would be less than 10 K at 1 kHz, given a typical barrier height for the chloromethyl rotor. However, the data revealed broader features, indicating that the rotors contained a range of barrier heights.

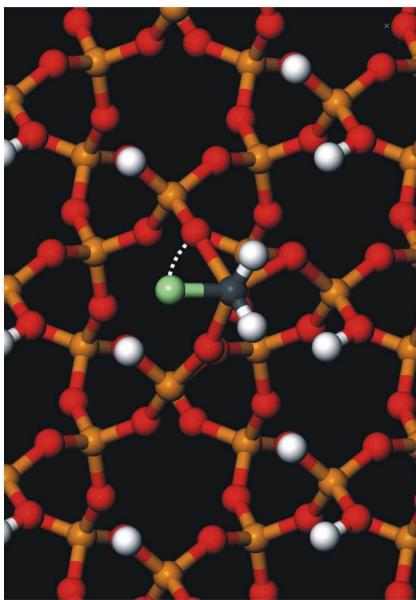


Figure JP1. Chloromethyl group attached to a fused silica substrate. The polar chloromethyl group rotates about an axis perpendicular to the page.

To better understand this result, we performed molecular dynamics calculations of the rotational potential for chloromethyl rotors on quartz glass. For ten sites on which the chloromethyl molecule was placed, a wide distribution of well and barrier energies was observed. The breadth of the distribution indicates that the intrinsic torsional potential, which is equal for all rotors, is superimposed with a surface interaction potential, which depends on the surrounding environment. The dielectric data was fit by a distribution of Debye relaxation peaks, and we compared the rotor barrier height distribution inferred from a fit to the dielectric data to the barrier height distribution obtained from the simulations. Generally, the calculations and experimental measurements agreed, although for the chloromethyl rotors the calculated distribution is shifted by about -0.5 kcal/mol as compared with the distribution found from dielectric measurements.

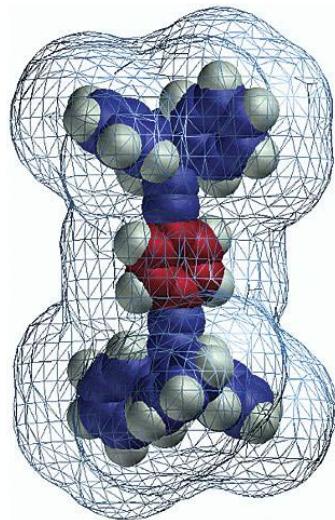


Figure JP2 UCLA phenylene rotor molecule.

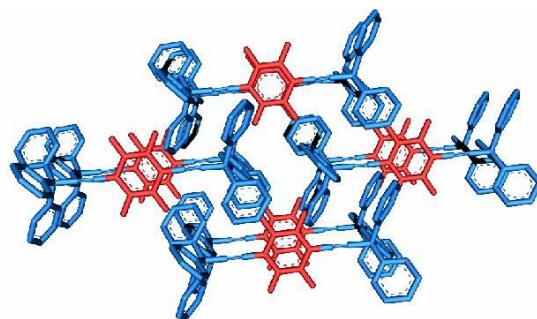


Figure JP3. Crystal structure of phenylene rotor arrays showing proximity between rotary element (red) and the crystal lattice.

Phenylene Rotor Molecular Crystals (*Robert Horansky, Erick Winston, Matt Myers*)

We have used bulk dielectric spectroscopy to characterize rotations and rotor-rotor interactions in phenylene molecular rotor crystals made by Miguel Garcia-Garibay and his collaborators at UCLA. These molecules contain a rotating polar phenyl group attached by triple bonds to bulky end groups (see Fig. JP2). In the crystalline environment rotation proceeds by thermal hopping over a potential barrier dominated by steric interaction between the rotating group and the end groups of an adjacent molecule, as can be seen in Fig. JP3. The symmetry of the local environment gives rise to an asymmetric potential for monofluorophenylene rotors and a symmetric potential for difluorophenylene rotors (Fig JP4). The dielectric signatures of the thermal rotations are easily observed in both cases, and are absent in non-polar analogs. Dielectric loss peaks for the diflouro crystal are shown in Fig. JP5. A nearly ideal single-exponential relaxation is observed with a barrier height of 14.1 kcal/mole and a well asymmetry of 0.93 kcal/mole.

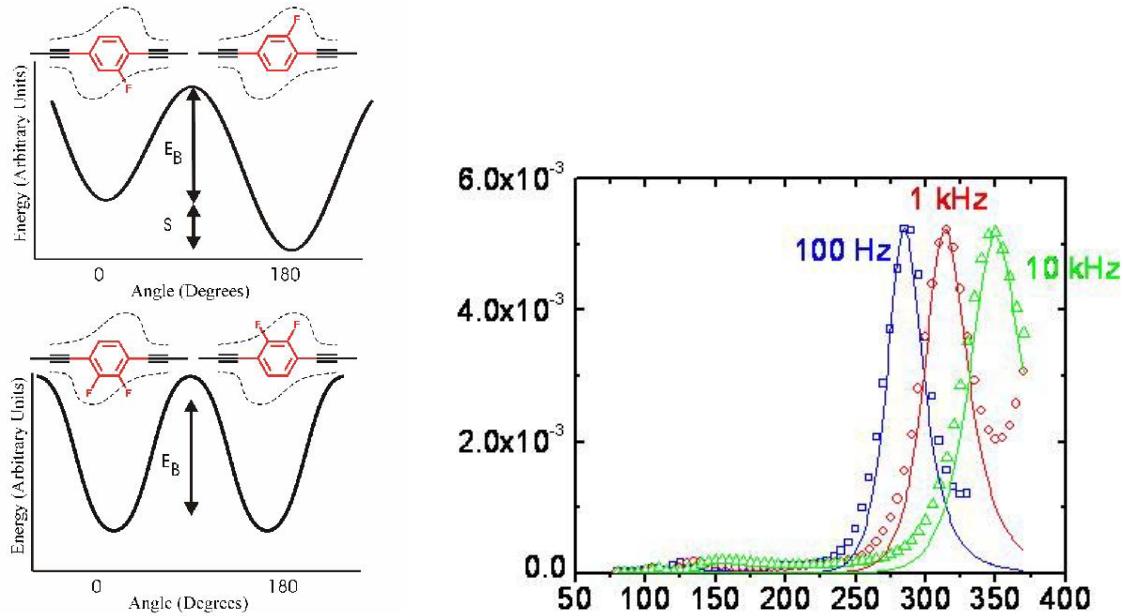


Figure JP4. (*left*) Local environment of rotor in phenylene rotor crystals.

Figure JP5. (*right*) Dielectric loss versus temperature and frequency for difluorophenylene rotor crystal.

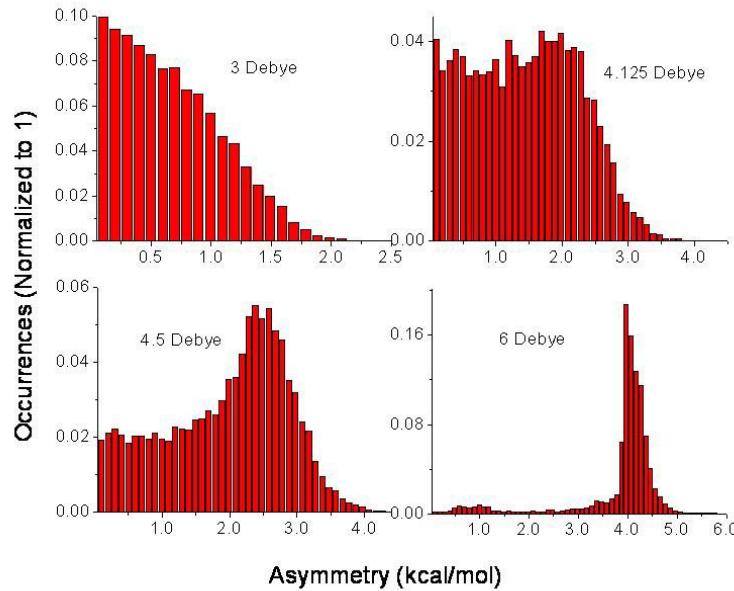


Figure JP6. Monte Carlo results for the local potential asymmetry at 300 K for several values of the rotor dipole moment.

The well asymmetry for difluoro crystals is smaller than for the monofluoro case, as expected, but it is not zero as would be inferred from the symmetry of the local environment given by the x-ray structure. Much of our effort was directed at understanding the cause of the asymmetry in the difluoro case. The two possibilities we considered were static disorder and rotor-rotor interactions. Data from small single crystals are very similar to data from

microcrystalline drop-cast samples, so it seems unlikely that static disorder can be the cause. However, the x-ray structure shows equal rotor populations in the two orientations, and thus it is averaged over rotor orientations. If the rotors interact, the unaveraged potential can be asymmetric. Several calculations were performed to better understand the effect of interactions. Results of a finite temperature Monte Carlo simulation of the interacting rotors are shown in Fig. JP6. The histogram shows the distribution of well asymmetries at 300 K for several values of the rotor dipole moment. When the dipole moment is large the rotors order into ferroelectric planes with an antiferroelectric arrangement from plane to plane. In the ordered state the histogram shows a sharp peak because every rotor is in the same environment. The data in Fig. JP5 correspond well with the distribution predicted at 4.5 Debye, a case where rotor-rotor correlations are weak and there is a wider distribution of asymmetries. This value of the dipole moment is somewhat larger than the actual value of 3 Debye. We conclude that rotor-rotor interactions are the likely cause of the observed asymmetry, but the strength of the interaction is enhanced over the dipole-dipole value, probably due to indirect steric interactions between rotors.

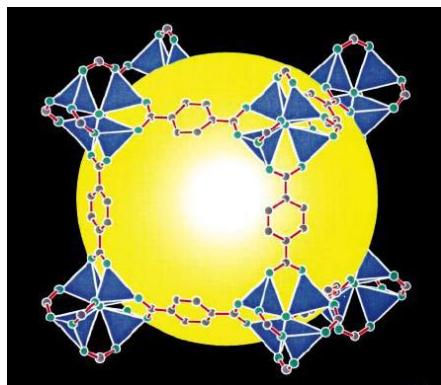


Figure JP7. MOF-5 structure shown with non-polar rotors on the cube edges.

Metal Organic Framework Crystals (*Erick Wintson, Peter Lowell*)

Certain MOF structures are of extremely low density and high porosity, and as such have attracted interest as substrates for gas adsorption, including hydrogen storage. However, the high porosity of these structures also make them interesting for incorporating molecular motion, including molecular rotors. MOFs containing polar molecular rotors could be useful as novel electronic and electro-optic materials, including solids with liquid-crystal-like electro-optic properties. The system we have chosen for experiments on molecular rotation is known as MOF-5 (discovered and elaborated upon by Yaghi and collaborators), Fig. JP7. This is an octahedrally connected cubic structure with roughly 80% of its volume empty, as depicted by the sphere in figure.

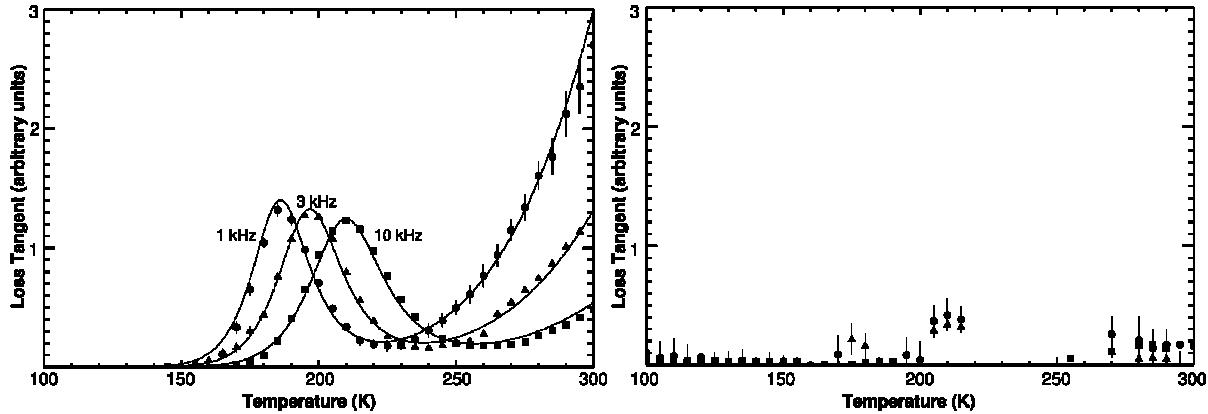


Figure JM8. *left* Dielectric response for mono-brominated MOF-5 in the temperature range 145-300 K fit to a single Debye function with a high temperature ionic conductivity term. The fit indicates a barrier to rotation of 7.5 kcal/mol and an asymmetry of less than 0.2.

Figure JM9. *right* Dielectric response for the non-polar MOF-5 structure. No loss peaks are observed. It is believed that the small discontinuities in the data are due to temperature induced shifts of the crystals in the capacitor.

For our experiments we have crystallized a mono-bromo substituted terephthalic acid linked version of the MOF-5 structure shown in the figure, as well as the unmodified non-polar MOF-5 structure. Several small crystals of cubic morphology were placed in a bulk capacitor for dielectric measurement and X-ray spectra were taken on samples to confirm crystal structure. Figures JM8 and JM9 show a clear peak near 200 K for the brominated benzene crystal but no peak for the un-brominated benzene crystal. The Br-MOF-5 curve fits very well to a single exponential relaxation time constant which indicates that long range dipolar interactions are not significant at this temperature. In the future we hope to compare the observed rotation barrier height to calculations and to extend these measurements to an amino-substituted MOF-5.

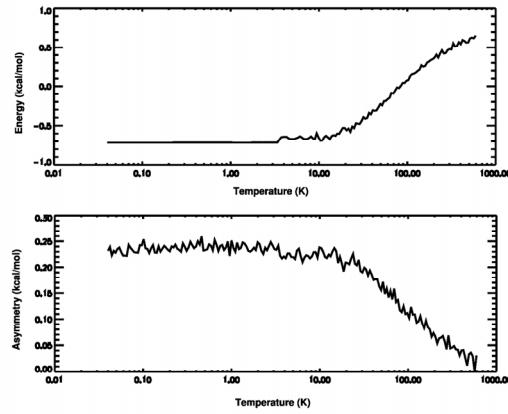


Figure JP10. Energy and well asymmetry from a Monte Carlo simulation of Br-MOF-5.

To confirm the insignificance of dipolar interactions near 200 K for Br-MOF-5 a Monte Carlo simulation was performed with periodic boundary conditions at one unit cell (each containing 24 dipoles) and long range dipolar interactions handled by Ewald summation. Figure JP10 shows the total interaction energy of the unit cell and the average well asymmetry of randomly chosen dipoles as a function of temperature. As the temperature is lowered the energy decreases indicating the onset of ordering and thereby creating a situation with asymmetric wells. Near 200 K, the simulation indicates an asymmetry of ~0.06 kcal/mol which is less than can be determined from the dielectric spectra. To observe the effects of long range dipolar interactions by dielectric relaxation it appears necessary to synthesize structures with lower rotational barriers or higher dipole moments. Efforts in this direction are planned for the future.

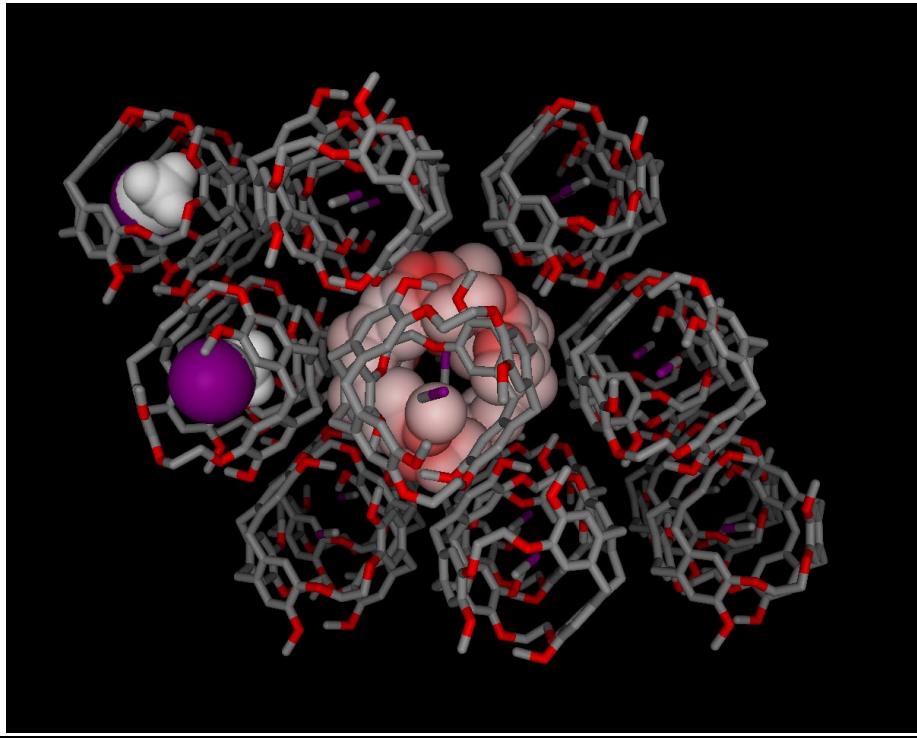


Figure JP11. Iodomethane in cryptophane-A from X-ray spectroscopy.

Cryptophane Molecular Crystals (*Erick Winston, Peter Lowell*)

Cryptophanes are a class of molecule with an interior cavity which can be occupied by smaller guest molecules non-covalently. In cases where the guest molecules are free to tumble within the cryptophane host, and where the cryptophanes can be crystallized, it is possible to create ordered arrays of reorienting guest molecules. By using small dipolar guests, such as the methyl halides, the guest motions can be observed by dielectric spectroscopy and guests may order via strain or dipole-dipole interactions. For the case of iodomethane in cryptophane-A, the observed rotational barriers were compared to computational molecular mechanics calculations of iodomethane in an artificially symmetric cryptophane host. Using the X-ray structure for iodomethane in cryptophane-A Fig. JP11 the molecular mechanics calculations were repeated with this more accurate host-guest environment as well as for crystallized chloroform in cryptophane-A. The potential surfaces for these systems are shown in Figs JP12-JP13. In the contour plots we have adopted planetographic coordinates where the prime meridian is defined by the line passing through the centers of position of each of the CTV units of cryptophane. Due to the openings between ethyl linkers it is expected that these are the directions in which the long arms of the guest will want to point. For CHCl_3 this corresponds to the dipole aligning with the meridian and the three chlorines pointing to each of the three openings. It is tightly bound to this orientation with a ~40 kcal/mol barrier to rotation. CH_3I , in contrast to CHCl_3 , wants to have its dipole axis lying in the equatorial plane. Figure JP14 shows the potential energy CH_3I experiences along the minimum energy equatorial band. The six maxima are probably due to putting an approximately $\text{C}2$ symmetric guest in a approximately $\text{C}3$ symmetric host; neighboring maxima correspond alternately to whether the iodine or carbon end of the dipole is closest to the ethyl linkers around the equator. Future work will be focused on crystallizing

chloroform in cryptophane -- a suitable system for dielectric measurements to compliment the iodomethane data and compare to the molecular mechanics potential surfaces.

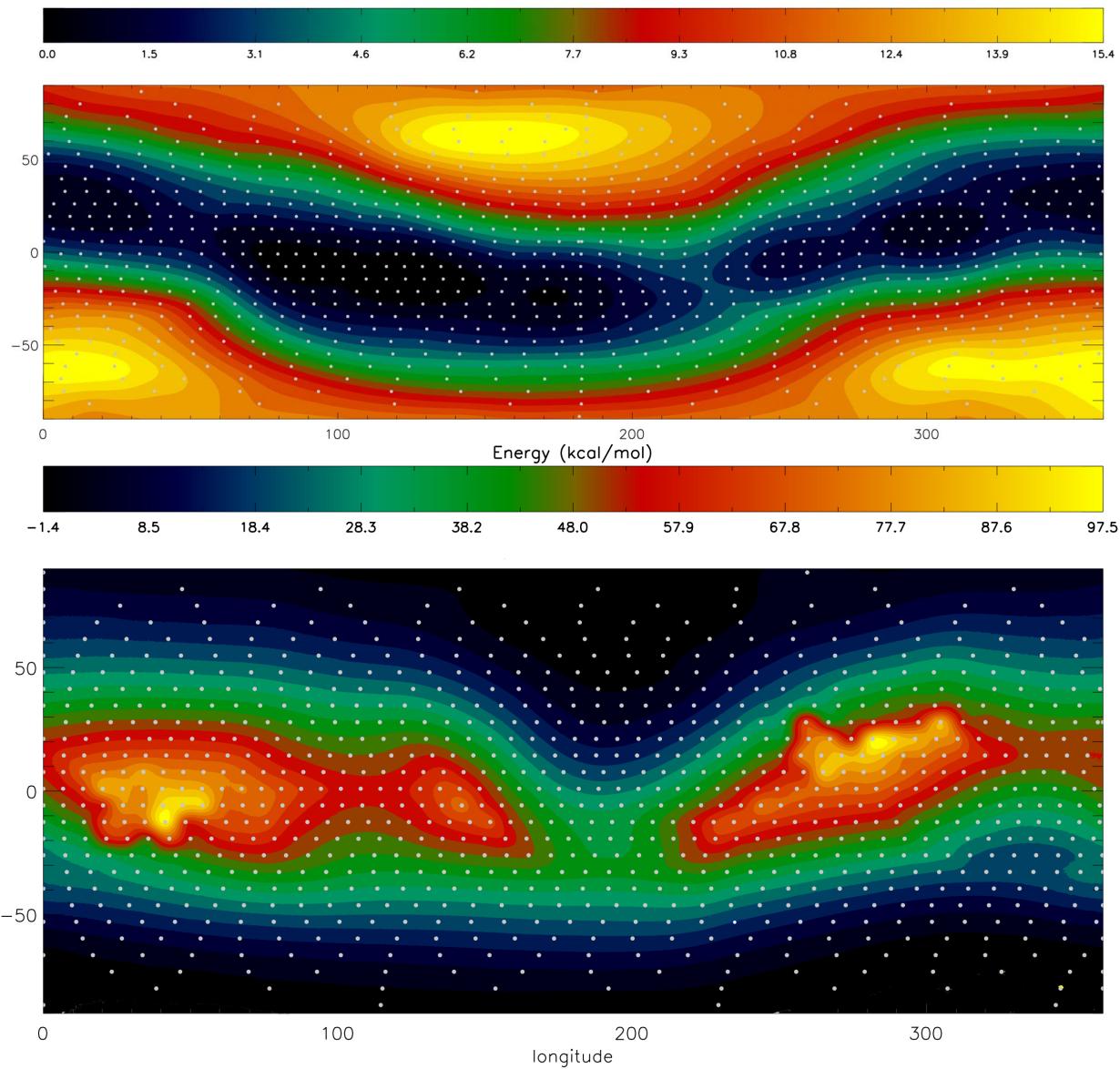


Figure JP12 (top) and Figure JP12 (bottom). CH_3I (top) and CHCl_3 (bottom) in cryptophane-A: orientational potential energy surfaces of host-guest system. Grey dots indicate the points where the energy was actually evaluated. The rest of the points were approximated to these with a minimum curvature spline.

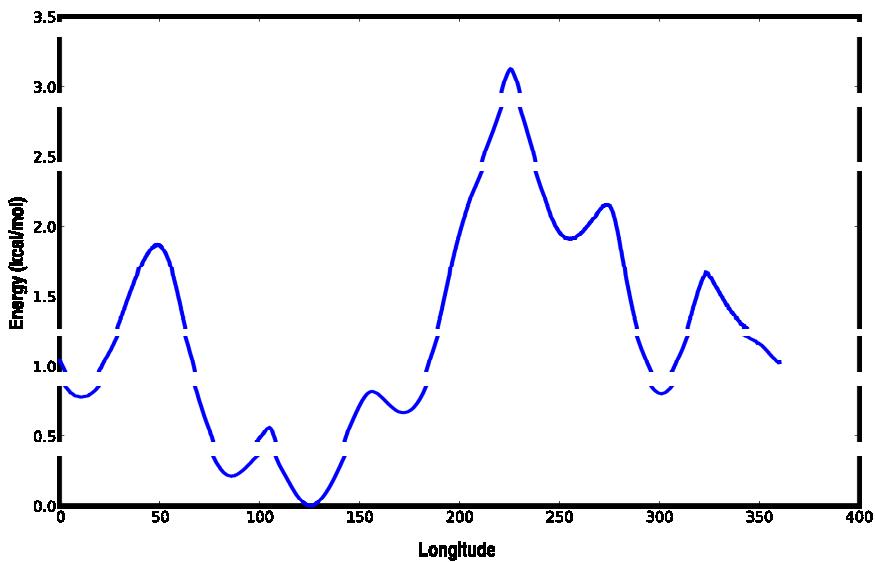


Figure JP14. Orientational potential energy of CH₃I in cryptophane for equatorial orientations.

Surface Dielectric Spectroscopy in UHV (*Jason Underwood*)

We are currently studying the dielectric response of disordered 2-dimensional arrays of dicarbonylchloro(pentamethylcyclopentadienyl)iron (see Figure JP15) molecular rotors. To resolve the small (10^{-5}) loss tangents that result from monolayer and sub-monolayer coverages, ratio-transformer bridge methods are being used at audio frequencies and over the temperature range $4 \text{ K} < T < 400 \text{ K}$. Rotor molecules are deposited from a near-ambient effusion cell onto Ar⁺ sputter-cleaned fused silica substrates, which are lithographically patterned with Au interdigitated electrodes. Deposition and subsequent dielectric measurements are performed *in situ*, in an ultra-high vacuum (10^{-9} Torr) environment. X-ray photoelectron spectroscopy (XPS) measurements are also performed *in situ* to provide independent confirmation of surface chemical species and rotor coverage.

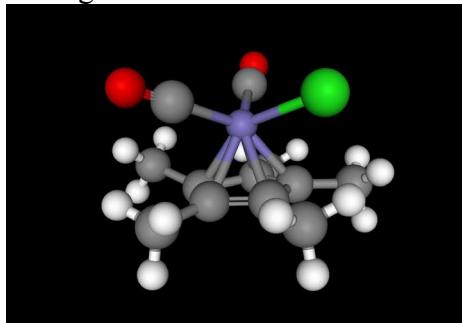


Figure JP15. Ball and stick model of dicarbonylchloro(pentamethylcyclopentadienyl)iron rotor. Atoms are colored as follows: H (white), C (gray), Fe (violet), Cl (green), and O (red). The base consists of the 5-membered C ring, and the two carbonyl groups and the C ring, and the two carbonyl groups and the Cl atom form the dipolar rotator.

The cyclopentadienyl rotor does not contain any labile groups, and so its attachment is facilitated by van der Waals attraction with the substrate surface (i.e., physi-sorption). Evidence of rotor desorption was observed in both the dielectric and photoemission spectra, indicating reversible control over the substrate coverage. Desorption was found to occur around $T_{\text{desorp}} =$

220 K. Ongoing work includes dielectric measurements to 4 K of dilute arrays, to resolve the expected Debye peak at $T \sim 20$ K, and growth and characterization of arrays with coverages between the dilute and monolayer limits. Future work will be focused on ordered 2-d arrays of a different molecular rotor system.

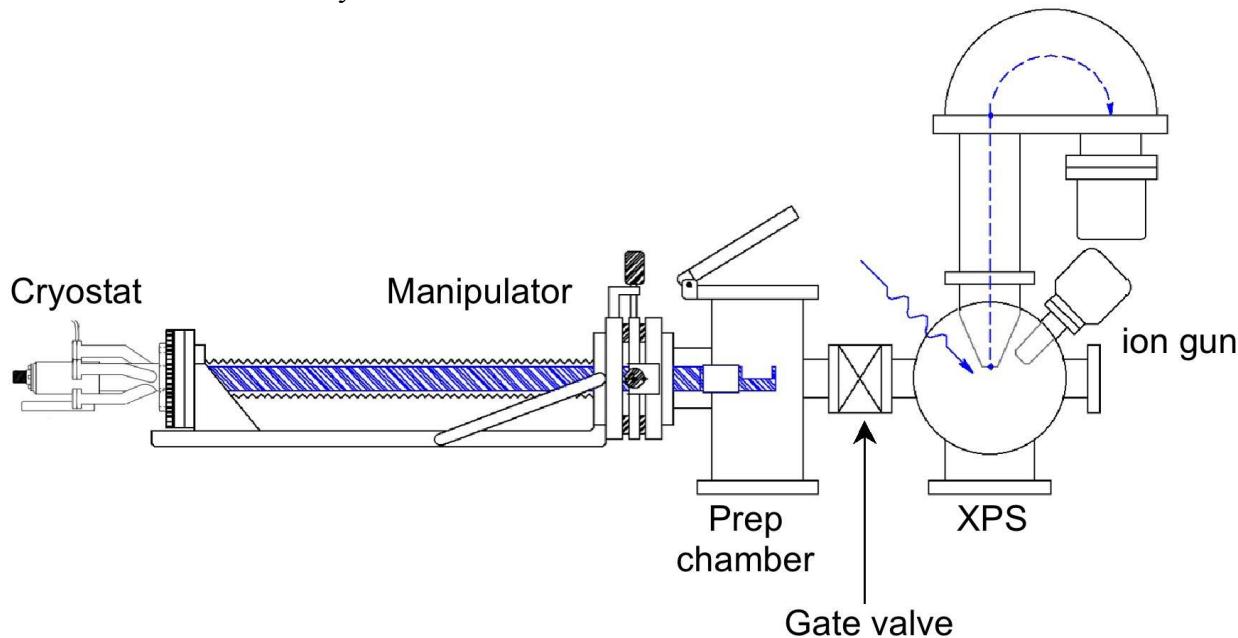


Figure JM16. Schematic of the experimental apparatus for UHV dielectric studies.

The UHV system consists of a cold finger (4 – 500 K) mounted on a manipulation stage that permits x,y,z translation and rotation about the cold finger axis, a preparation chamber, and the XPS analysis chamber (see Figure JP16). The nominal pressure in both chambers is 1×10^{-9} Torr. The system was designed to allow sample transfer *in situ* between prep chamber and XPS without changes in sample temperature. Also, the rotational capabilities allow for variable-angle XPS, which gives a non-destructive depth profile of the specimen surface. In mid-2005, we began to make the first measurements of rotor systems. The particular metal-organic rotor being studied highlights the capabilities of the UHV system. Unlike the rotor molecules our group has studied previously, which chemically react with OH groups on the substrate surface, this rotor attaches to the substrate by physi-sorption (i.e., van der Waals interaction). It has a large dipole moment (~ 1 Debye) and is expected to have a low barrier to rotation (~ a few kcal/mol), which may provide a facile route to study quantum effects, or the effects of rotor-rotor interactions.

Rotor molecules are synthesized by our collaborators (Josef Michl et al.) and supplied in the form of small rod-like crystallites. These crystals are placed into a stainless steel crucible, which is then attached to a near-ambient effusion cell (NEAC). The NEAC is differentially pumped, and is attached to the prep chamber through a gate valve, to allow changing of the crucible without breaking vacuum in the prep chamber. Deposition is accomplished by opening the valve while maintaining the substrate at low temperature (< 250 K). The van der Waals (vdW) attachment allows us to reproducibly deposit and remove rotors *in situ*, by adjusting the temperature above or below the gas desorption temperature. This effect was observed in both the dielectric data and the XPS spectra.

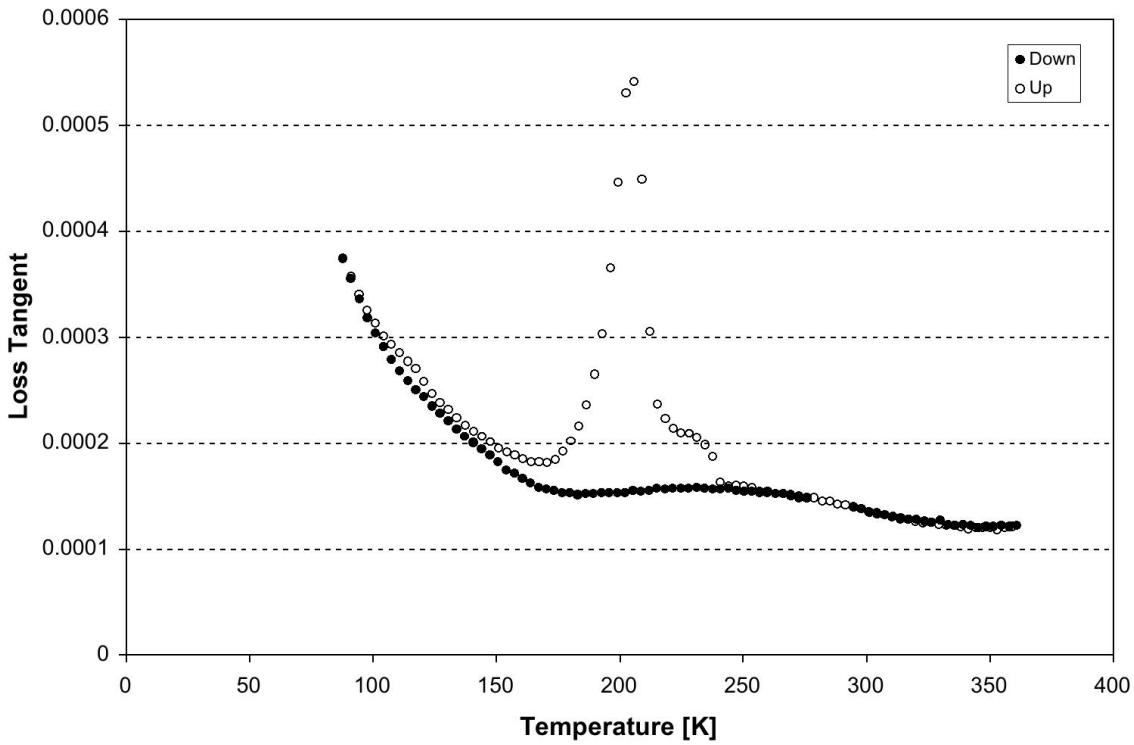


Figure JM17. Dielectric response of the cyclopentadienyl rotor for $T > 80$ K, showing rotor desorption at 220 K.

Figure JM17 shows the dielectric loss during rotor vapor exposure. Starting at $T = 360$ K, the temperature is ramped down to 80 K, and then back up again. During the down sweep, rotor molecules slowly fill the very narrow gap between the microelectrodes. Due to the low partial pressure of the rotor vapor, the loss tangent does not change appreciably during the 5 minutes or so between measurements. However, it takes about 10 hours to sweep down from 250 K and back again. Over that timescale, a substantial number of rotors will have condensed. As the thermal energy $k_B T$ approaches the VdW energy, the rotors start to become mobile and move around within the gap ($170 \text{ K} < T < 220 \text{ K}$). This motion manifests itself in the sharp loss peak depicted in the figure. At still higher temperatures, the rotors leave the surface and the loss returns to the background of the substrate. An analysis of the kinetics during gas desorption is currently in progress.

The low barrier height of the cyclopentadienyl rotor means that the Debye peak will occur at temperatures ~ 20 K. Additional work will involve modifications to the cold finger to reach the low temperatures necessary to fully resolve the peak. We also plan to do additional experiments with varying rotor coverage to study the effects of rotor-rotor interactions. It is expected that a glass transition should occur at temperatures above the Debye peak, but below the desorption temperature.

Rogers Contribution

We have pursued nonlinear surface second harmonic generation (SSHG) measurements since the beginning of DURINT funding of our work on surface mounted rotor molecules. SSHG arises from nonlinear motion of electrons near the surface, is sensitive to surface localized molecules, and can be performed on any surface or interface that can be reached by the incident light field. As a surface science tool, it has the advantage of not requiring vacuum environments. During the early parts of the project, we studied the SSHG of a variety of metallic and insulating substrates (see listed publications). In the second half of DURINT support, graduate student James Walker has continued our surface nonlinear optical studies of surface mounted dipolar rotor molecules, especially the difluoroanthracene rotor shown in Figure R1.

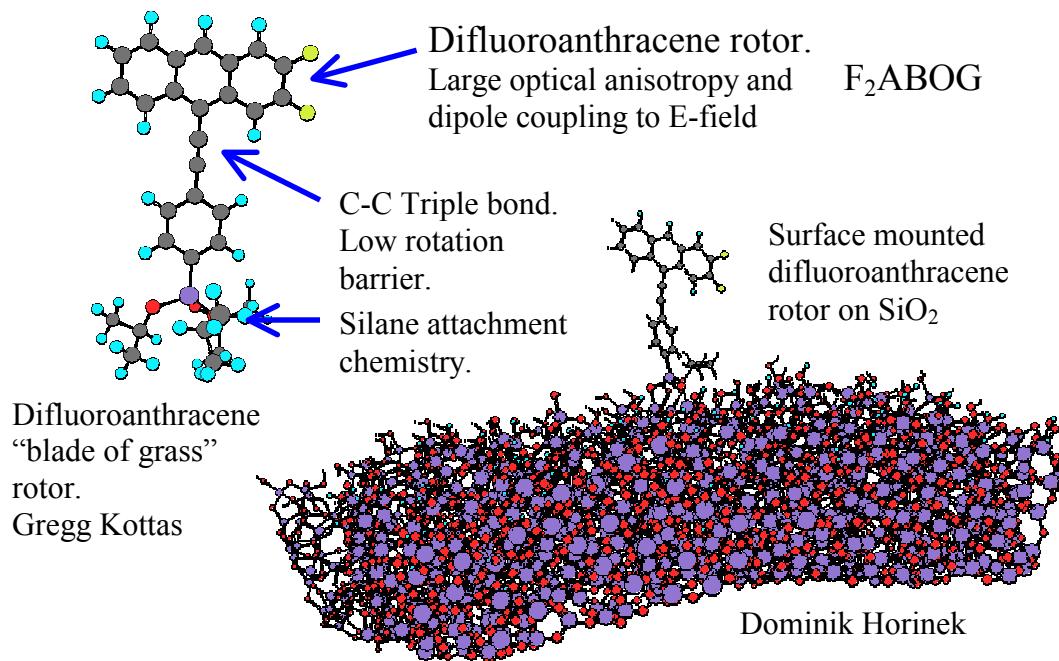


Figure R1. The difluoroanthracene-based surface rotor molecule is a prototype rotor system that we are studying. The upper left shows the molecule as synthesized with isopropoxy silane attachment feet, while the lower right shows a molecule surface mounted on silica with two of the three feet reacted for attachment. The molecule was synthesized by Gregg Kottas in Prof. Josef Michl's lab. Molecular modeling was done by Dominik Horinek in the Michl Lab.

Nonlinear optics, especially surface second harmonic generation (SSHG), has long been known to be a particularly useful tool for studying molecule orientation at surfaces and interfaces [1, 2, 3, 4]. Optical second harmonic generation is described macroscopically by a third-rank second harmonic susceptibility tensor, $\tilde{\chi}^{(2)}$, which converts two applied electric field vectors into a second harmonic polarization vector:

$$P_i^{(2)} = \chi_{ijk}^{(2)} E_j E_k$$

As for any third-rank tensor, this second order susceptibility is forbidden in systems with inversion symmetry. Therefore, e.g. cubic or isotropic media will not normally generate second harmonic light. However, any surface is inherently a region of broken inversion symmetry. Therefore, second harmonic can be generated at any surface or interface between dissimilar media. Shen and his co-workers [2] have shown how to use surface second harmonic generation to provide information about the orientation of molecules localized at surfaces. The approach is to first use a combination of input and output polarization geometries to measure $\tilde{\chi}^{(2)}$, to then relate the measured result back to the local molecular hyperpolarizability tensor, $\bar{\alpha}^{(2)}$, the average molecular orientation, and molecular surface density, N_s via the relation:

$$\chi_{ijk}^{(2)} = N_s \sum_{\xi, \eta, \zeta} \langle (\hat{i} \cdot \hat{\xi}) (\hat{j} \cdot \hat{\eta}) (\hat{k} \cdot \hat{\zeta}) \rangle \alpha_{\xi \eta \zeta}^{(2)}$$

This process is feasible primarily for molecules where the hyperpolarizability is known, or where either the molecular symmetry or a resonance condition causes the tensor to be dominated by only a few elements. For example, for a hypothetical cylindrical molecule with a symmetry axis along the ζ axis, the 27 element tensor is populated with only two values, $\alpha_{\xi\xi\xi} = \alpha_{\zeta\zeta\zeta} = \alpha_{\eta\eta\zeta} = \alpha_{\eta\zeta\eta}$, and $\alpha_{\zeta\zeta\zeta}$. In the unusually simple case where $\alpha_{\zeta\zeta\zeta}$ dominates, typically due to proximity to a resonance, then ratios of the measured susceptibility tensor elements can be used to determine the average value of $\cos \theta$ and $\cos^3 \theta$, where θ is the angle between the surface normal and the ζ axis of the molecules [2, 4].

In the third and fourth years of funding, we determined that the difluoroanthracene rotor surfaces show second harmonic generation that differs substantially from bare substrates in the spectral region where anthracene is strongly absorptive in linear optics. These results indicate that the molecular hyperpolarizability is making a contribution to the reradiated second harmonic light. The final year, we have continued the systematic study of the second harmonic from surfaces of this molecule, to determine the details of how the molecule contributes to the SSHG. Figure R2 shows a compilation of spectral data for the difluoroanthracene rotor on silica along with a solid line fit to a model where the second harmonic is generated by an interfering combination of a wavelength independent background (assumed to arise from the silica substrate) and a single resonant molecular contribution to the hyperpolarizability.

These results suggest that the observed SSHG, while not completely dominated by the molecular hyperpolarizability, can be well understood as a molecular contribution in the presence of a substrate background. We have prepared clean silica substrates in the UHV/optical spectroscopy apparatus (constructed with separate DURIP funding), have verified the flat spectral response of silica.

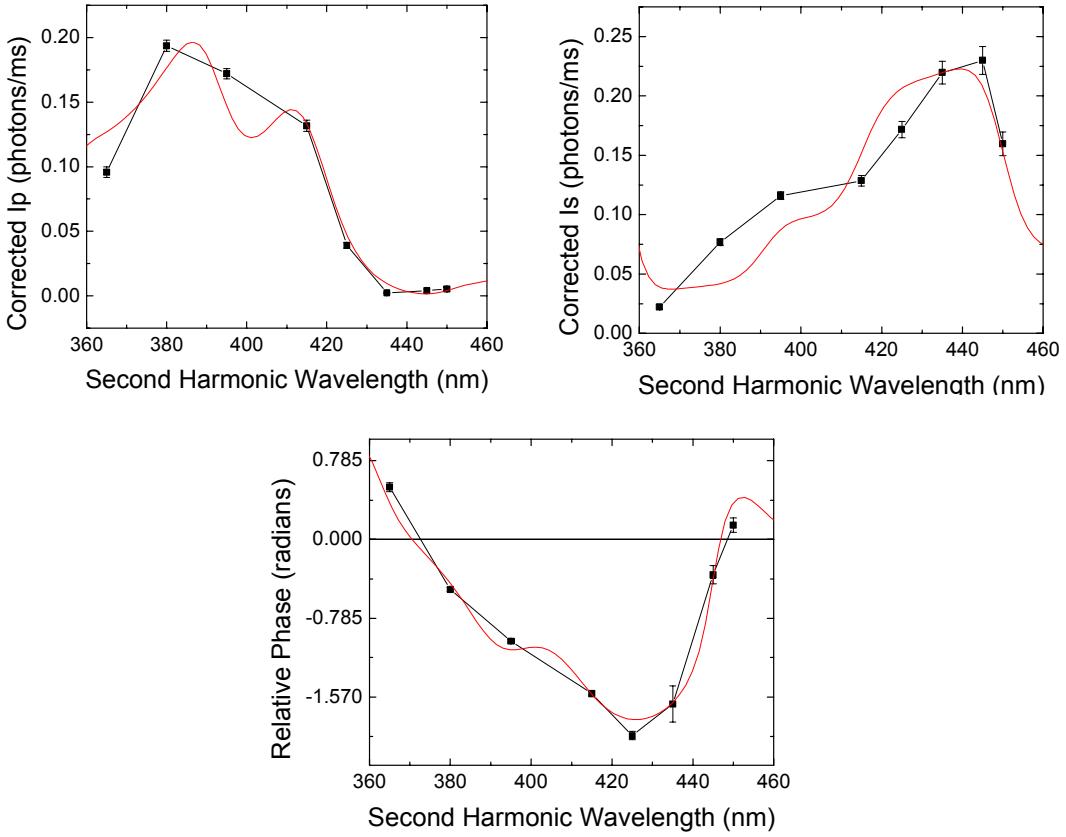


Figure R2. Plots of p-polarized intensity (I_p), s-polarized intensity (I_s), and their relative phase versus wavelength. The red lines are a fitting of the data to a model with a vibronically broadened absorption structure interfering with a wavelength independent background. The model shows that a molecular absorption appropriate for anthracene, along with a substrate background contribution, explains the observations well.

In the final part of our work, Jim Walker setup a bank of high speed MOS-FET switches to apply faster high voltage pulses. The use of higher speed voltage pulses expand the time scales over which we can look for interesting molecular dynamics. Figure R3 shows oscilloscope data of an applied 300V pulse with less than 10 nanosecond characteristic rise time. Previously, we have shown that the difluoroanthracene rotor surfaces show SSHG electro-optic effects that are independent of frequency up to roughly 1 kHz. In other words, whatever combination of electric field induced rotation and distortion that is occurring on the surface, it occurs on time scales that are at least as fast as 1 millisecond. With the new high voltage switches, we can now apply electric field steps and pulses with a few nanosecond time variations. We applied this capability to study the time response of substrates with mono layer difluoroanthracene rotor surfaces.

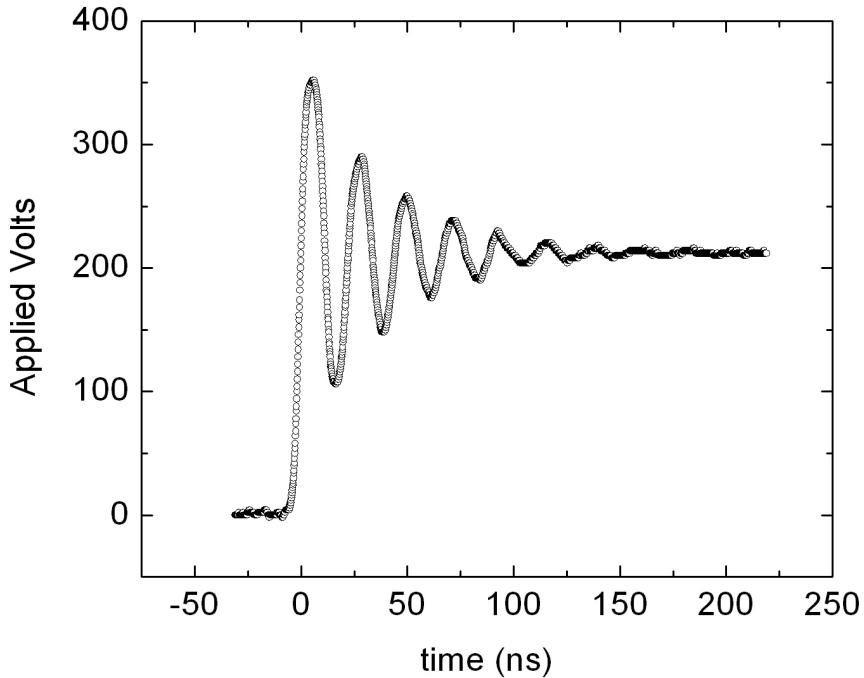


Figure R3. Oscilloscope trace showing the rising edge of a nominally 200 V step applied to coplanar capacitor electrodes. The initial rise time is less than 10 nsec.

Most recently, we have used a multi-channel analyzer to acquire photon counts and time synchronize them with the applied voltage pulses to look for voltage induced electro-optic changes in the surface second harmonic generation. In these experiments, the voltage pulse is applied to a coplanar capacitor structure with a 500 micron gap on silica. Therefore, the associated electric field strengths are on the order of 1 Volt/micron. We then treat the silica substrate with difluoroanthracene rotor (see figure R1) to mount the rotors between the electrodes. Ellipsometry suggests that we are preparing roughly half monolayer coverage layers in the capacitor gap. Application of the voltage induces anisotropy in the surface layer, and causes associated changes in the total surface second harmonic generation.

In Figure R4, we show correlated photon counts from a difluoroanthracene rotor surface as a function of time during the application of a fast voltage pulse on the capacitor electrode structure. We have studied pulse response of this type for a large number on input polarization conditions, in different spectral regions, and with applied voltage directed both in and perpendicular to the optical plane of incidence. All of these measurements confirm a significant electro-optic effect, synchronized with the voltage pulse, and clearly arising from the difluoroanthracene optical spectrum.

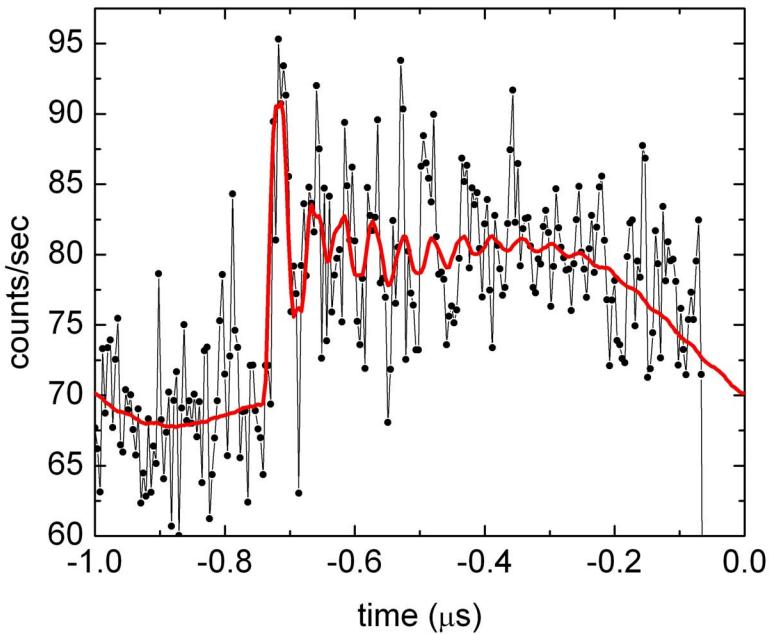


Figure R4. Example of measured SSHG photon counts in response to an applied 400 volt peak voltage pulse. The voltage signal is repeated at a 1MHz rate. The rise time on the initial voltage pulse is roughly 10 nanoseconds. The measured voltage pulse has been scaled and superposed as a red line on the photon counts to show that for this optical geometry, the electro-optic effect is linearly related to the applied voltage. The electro-optic effect on this time scale is prompt.

We also find that the magnitude of this response is unchanged as we go from static applied voltages, to millisecond time scale pulses, to the fastest pulses of several nanoseconds. In other words, the difluoranthracene surface can respond fully to voltage pulses on the 10 nanosecond scale. At the end of DURINT support, we are left with two possible explanations for these observations. First, it is possible that the rotor molecules move rather freely on the surface and are able to keep up with these electric fields with rather fast response times. Alternatively, the observed electro-optic effects are due entirely to changes in electronic polarizability, and the available 1Volt/micron field strengths are simply too small to cause any significant molecular rotation or motion. We note that liquid crystal systems often require a threshold electric field exceeding 5 Volt/micron before overall molecular motion will occur. Experiments at higher electric field strength require smaller gap capacitors and an associated reduction in illuminated area and associated photon counts. Still, we believe that such small gap structures are feasible and hope to pursue this line of research with future funding.

Optical/dielectric measurements of rotor-liquid crystal mixtures.

Graduate student Debra Krause has begun investigating 3-dimensional rotor systems, particularly a group of molecules produced in the laboratory of Prof. Miguel Garcia-Garibay at UCLA. The concept is to create a periodic array of sterically unhindered dipolar rotors, where the dipolar interactions may lead to polar ordering. In Figure R4 we show an example of one of Prof. Garcia-Garibay's molecules. On the left is an individual dipolar rotor molecule and on the right is the crystalline structure found from x-ray diffraction studies.

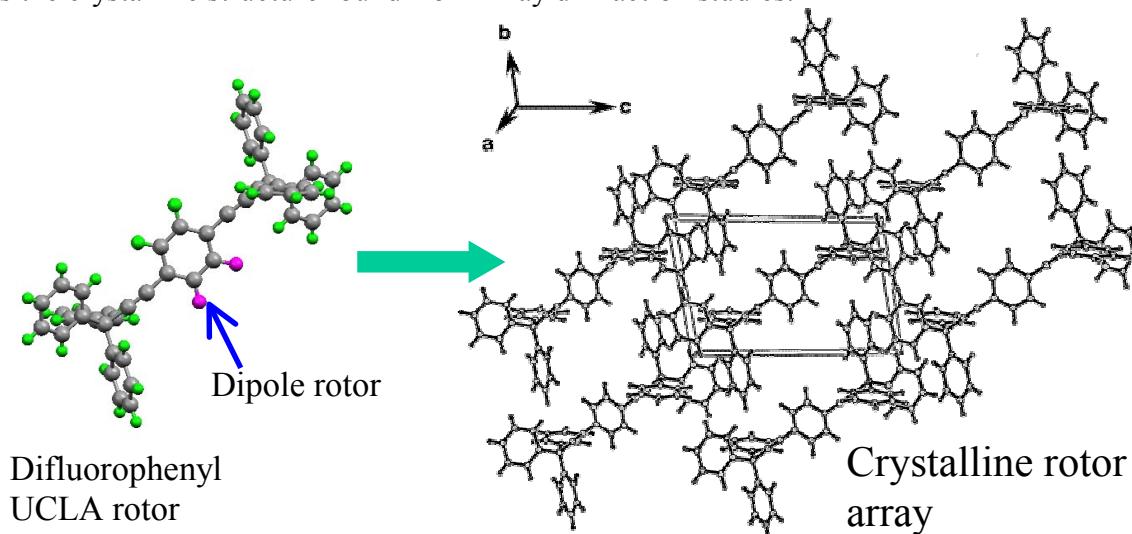


Figure R5. On the left is a model for an individual molecule of difluorophenyl UCLA rotor. On the right is shown the crystalline structure that this molecule takes on, as determined by x-ray diffraction studies [5].

In 3D crystals, the periodic structure occurs naturally (though without significant opportunity for adjustment or control) through crystallization. Joint studies of NMR line-shape (Garcia-Garibay), dielectric spectroscopy studies in the laboratory of Prof. John Price at CU-Boulder [6], and x-ray structural analysis (UCLA and CU-Boulder) demonstrate both the potential and the limitations of present crystalline rotor systems. For example, quantum chemical calculations for the molecule of Figure R5 demonstrate that the difluorophenyl rotor is extremely free to rotate in the isolated molecule. The rotational potential exhibits six to twelve potential minima depending on the orientation of the molecular ends, with potential barriers of roughly 100 calories/mole. Barriers of this height imply very small steric hinderance within the molecule and indicate that rotor orientation could be dominated by dipolar interactions. However, NMR line shape and dielectric spectroscopy agree that in the crystalline state, the rotor is restricted to one of two potential wells, with roughly 15 kilocalories/mole barriers between the wells. These barriers appear to arise from steric hinderance of rotor motion due to the foot sections of molecules in adjoining unit cells. The molecules appear to crystallize in an arrangement that leads to efficient space-filling and increased hinderance of rotor motion.

We have been investigating the use of liquid crystals for producing ordered rotor systems with decreased steric hinderance. The measurements use a combination of dielectric

spectroscopy, optical microscopy, and linear optical spectroscopy to investigate the behavior of liquid crystal and rotor mixtures. Our aim is to use liquid crystal ordering to produce environments where rotor motion can be less hindered. In Figure R6, we show one of the UCLA rotor molecules alongside the common liquid crystal molecule, TBBA.

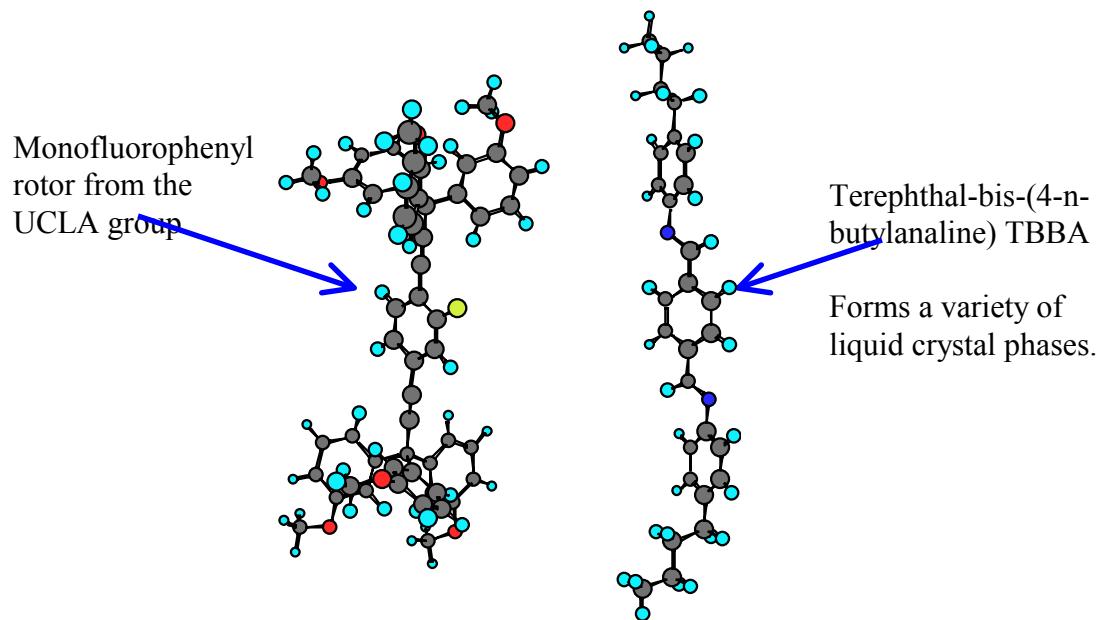


Figure R6. Comparison of the molecular structure of a UCLA monofluorophenyl rotor with TBBA liquid crystal molecule

TBBA is a heavily studied liquid crystal system, which shows a sequence of phase transitions from the isotropic liquid above 236 C, through nematic and then a variety of smectic phases below 200 C, finally becoming a crystalline solid below 113 C [7]. Under the assumption that the UCLA molecule (melting point roughly 120 C) dissolves into the TBBA system, it may be possible to find the rotor molecule aligned with the TBBA matrix so that the rotor portion is essentially free to move. A cartoon of this condition is shown in Figure R7.

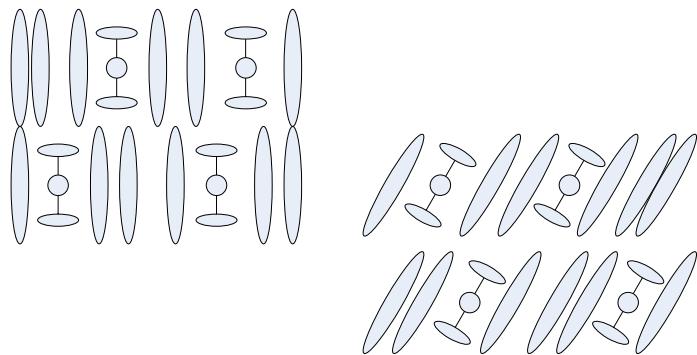


Figure R7. Schematic diagram of UCLA rotor molecules at modest concentration in TBBA smectic liquid crystal phases.

In this picture, the TBBA molecules align the UCLA molecules and prevent the steric hindrance due to neighboring UCLA feet. That such a cooperative assembly of the liquid crystal and rotor systems might happen very clearly depends upon the details of molecular interactions for specific rotor/liquid crystal pairs.

We have constructed a system for simultaneous optical microscopy and capacitance and dielectric loss spectroscopy. Commercial liquid crystal cells with transparent capacitor electrodes and liquid crystal alignment layers are used to study liquid crystalline order in mixed UCLA/TBBA systems, while the correlated dielectric measurements provide information about whether the rotors are moving differently in different environments.

In Figure R8 we show examples of an initial effort to dissolve a ratio of 1:9 monofluorophenyl UCLA rotor into the TBBA Smectic B phase below 150 C. The figure shows that the UCLA molecule is phase separated from the TBBA system into isolated islands of isotropic fluid, while the TBBA continues to show the appropriate texture for the smectic phase. The dielectric spectroscopy shows a single, nearly Debye loss peak that agrees well with the loss observed for pure UCLA molecule over this temperature range. The data are consistent with an inhomogeneous system of TBBA and UCLA molecule. We are continuing to investigate the solubility of various UCLA molecules in liquid crystal hosts in an effort to observe less hindered rotor motion.

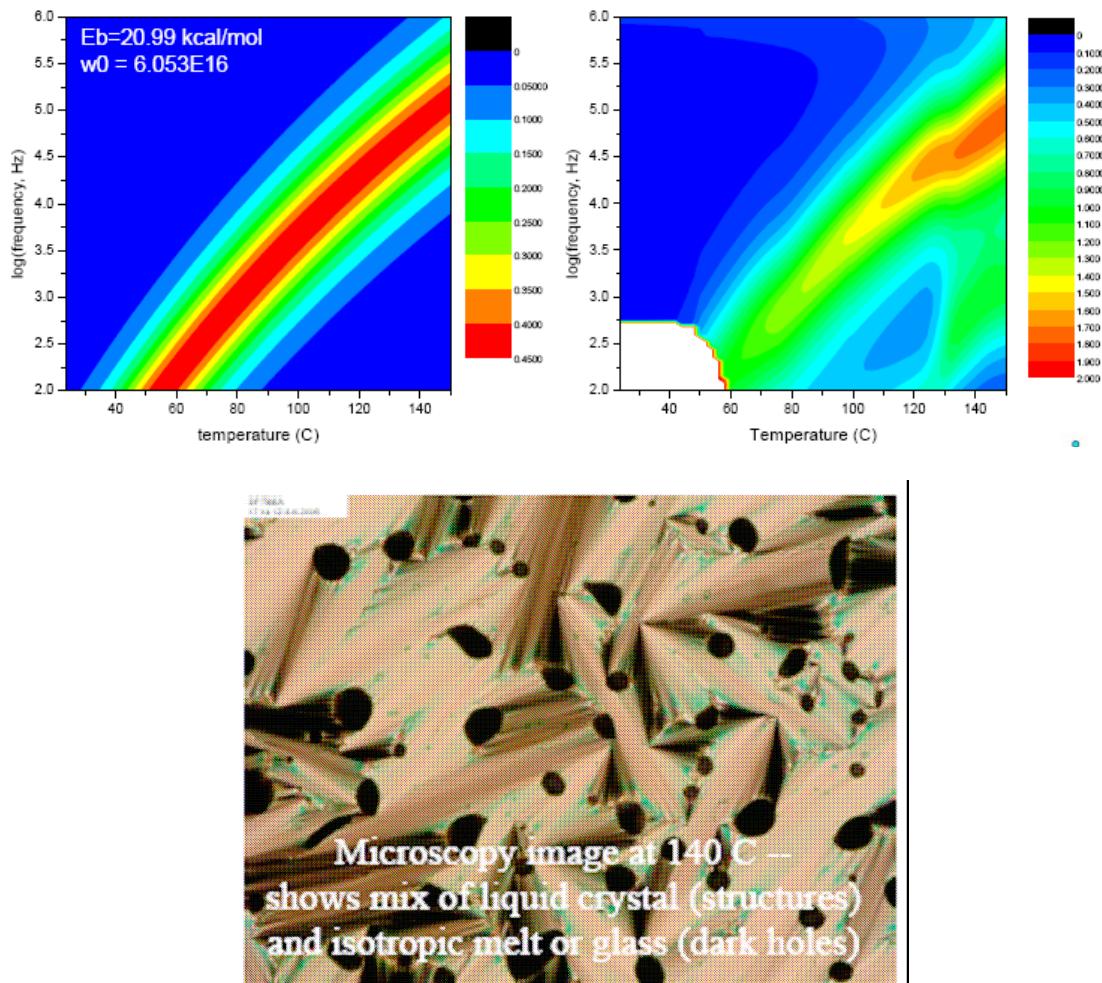


Figure R8. Simulated dielectric loss for a single Debye loss peak with a barrier of 21 kcal/mole and attempt frequency of 6×10^{16} Hz, measured dielectric loss of the UCLA/TBBA mixture consistent with this model and with pure UCLA behavior, and simultaneous optical microscopy that shows isolated islands of UCLA in TBBA i.e., failure to mix.

Adjustable molecular contacts

During this period, graduate student Shawn Tanner has investigated the use of electron-beam lithography to produce adjustable sub-micron electrical contacts, for eventual use in single molecule electrical conductivity experiments. This work is motivated by the possibility of measuring changes in molecular electronic transport due to the changes in molecular electronic states with different rotor orientations.

Figure R9 shows an SEM micrograph of a typical structure.

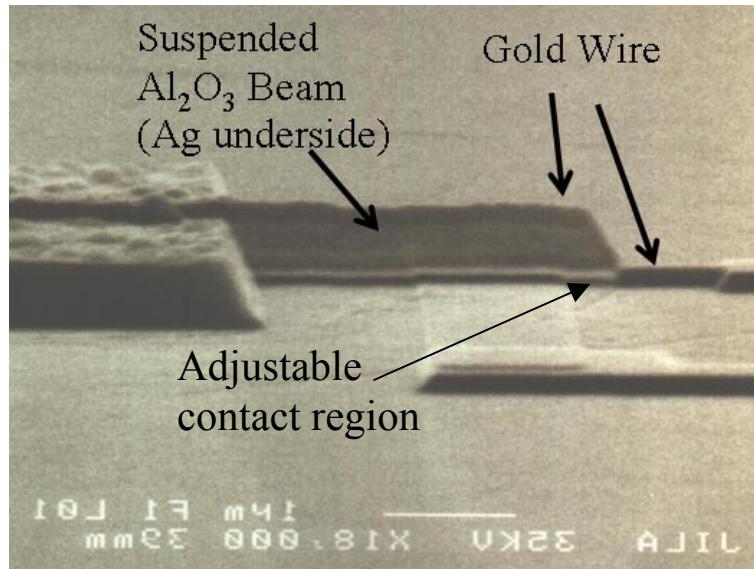


Figure R9. SEM micrograph of an adjustable metallic contact region. A gold wire is fabricated to bridge from the top of a freely suspended alumina cantilever down to the substrate. The cantilever can be moved by flexing the substrate, or by an electrostatic gate.

While adjustable tunneling is often observed in these structures, they are quite sensitive to the environment, often showing spontaneous fluctuations and sudden changes. Also, they show marked sensitivity to temperature changes. In an effort to better understand the behavior of the cantilever system, we have recently begun fabricating structures where the cantilever motion can be more directly studied by radio frequency electronic techniques.

Figure R10 shows two SEM micrographs of ‘hairpin’ cantilevers that we have recently fabricated. In these structures, each ‘hairpin’ is a pair of suspended simple cantilevers, with a suspended cross connection. Each of these structures carries a continuous wire from one side of the hairpin to the other.

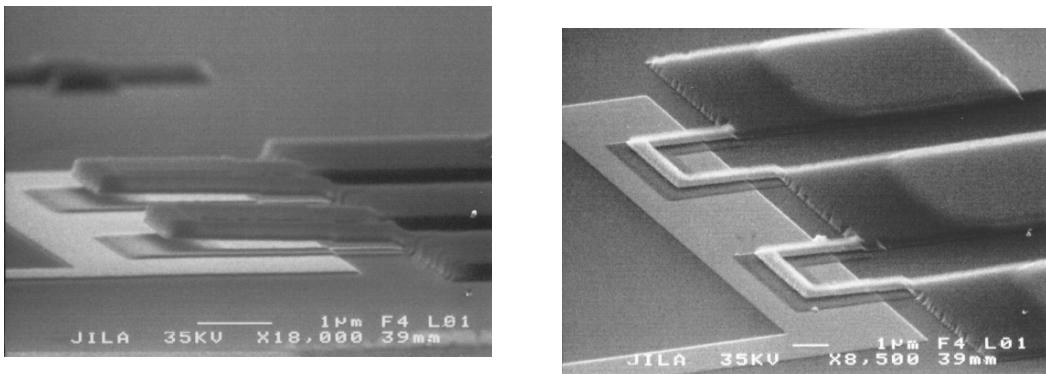


Figure R10. SEM micrographs of ‘hairpin’ cantilever pairs. Each cantilever carries a continuous wire on the underside. Motion of the cantilever is studied via the emf generated by motion in the presence of an applied magnetic field.

Cantilever motion can be studied by placing the cantilevers in a modest magnetic field (typically 0.2 Tesla from a pair of Cobalt-Samarium permanent magnets), embedding the cantilevers in an rf amplifier circuit, and measuring the small emfs generated by motion of the cantilever in the magnetic field. Figure R11 shows a schematic diagram of the rf readout system used to study cantilever resonances.

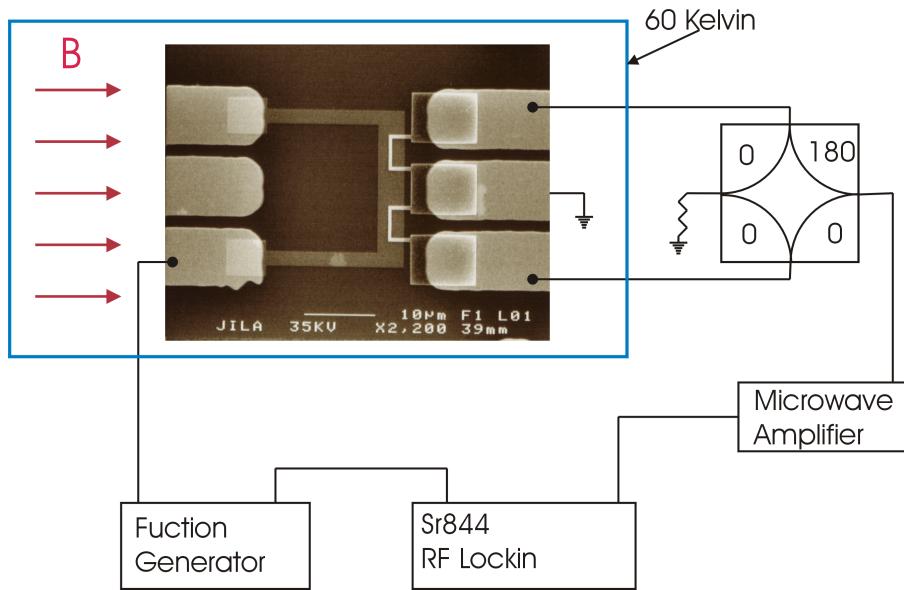


Figure R11. Schematic diagram of a hairpin cantilever pair with the rf circuit used to read out the emfs due to cantilever motion in a magnetic field. Cantilevers are operated in pairs to allow for balanced rf bridge measurements.

The cantilevers are studied in pairs that form matched ends of a resistance bridge. This geometry helps to match the devices to the rf electronics.

These cantilevers are observed to have mechanical resonance frequencies of several MHz, consistent with simple models for the structures. Figure R12 shows an example of the pair of resonances (one resonant line for each cantilever) near 5 MHz. By studying the dependence of resonant amplitude, position, and width on temperature and fabrication details, we hope to eventually construct more stable and usable adjustable contacts.

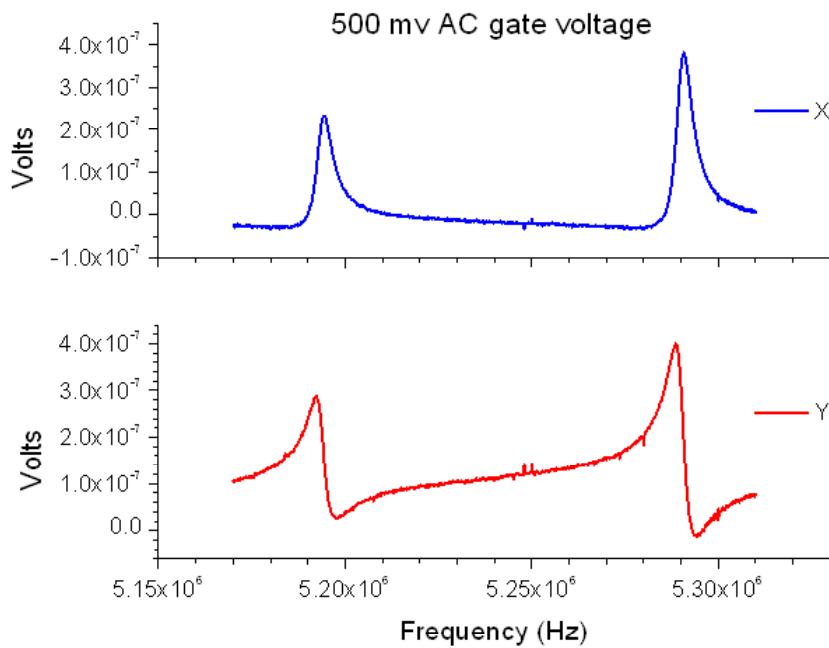


Figure R12. Real and imaginary parts of the measured emf from a hairpin cantilever pair. The cantilever resonances are found at roughly 5.2 MHz and 5.3 MHz, consistent with the predictions of modeling that includes the measured cantilever dimensions and the Young's modulus for alumina and silver.

Rogers References

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Ratner Contribution

As part of this extended MURI investigation into rotor arrays, computational and theoretical studies were carried out both at Northwestern (arrays of dipoles) and at a combination of Colorado and Prague (dynamics of single dipoles). These two modeling schemes were mutually supportive – the characteristics of the individual dipolar arrays, both as prepared experimentally and as calculated in Colorado, we used as input to the rotor array problems analyzed at Northwestern.

Northwestern work was done in collaboration with the group in Delft, and utilized classical dynamical simulation (both molecular dynamics and Langevin) to analyze both planar and linear dipolar arrays. The analysis included investigation of signal transfer in dipolar chains, signal speed in dipolar chains, effects of temperature on these situations, comparison with experiments, pulse-like signal generation and propagation, gate control of chain transfer and transport, proto-type logic elements (AND, OR), ordering effects, and switching characteristics following optical excitation.

Details of several of these have been given in the previous quarterly reports. Here we present some data on propagation of an initial photonic excitation, by transfer of dipolar orientation in linear, bent, and curved arrays of dipoles.

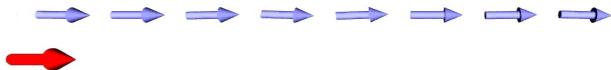


Figure MR1. Dipolar line, with external switch-controlling dipole

Figure MR1 shows a chain of dipoles, with a larger dipolar switching molecule nearby. Photo excitation of the larger dipole (which could be something as simple as para-nitroaniline) would form a very large local dipole (change of roughly 15 debye upon excitation). This would then couple by the dipole/dipole interaction to the nearby chain, and we have simulated how that chain would reorganize itself; eventually the very large dipole in the optically driven structure would cause the smaller dipoles within the chain to reverse their orientation. This dipole/dipole energy transfer would result in transduction of a signal with very high efficiency, once again not using any kind of electro magnetic interaction, but rather the simple dipolar interaction.

Our simulations show a number of characteristic behaviors. First, the mechanism by which the signal is transmitted is slightly counter-intuitive: one dipole rotates in a clockwise direction, and the next in the counter clockwise direction, before they are damped by thermal effects. The simulations here used Langevin dynamics, as is appropriate for signal transfer at reasonable temperatures. This is distinguished from some of the previous work done by us and by Rozenbaum, who studied only the zero temperature behavior. Here the thermal effects are very supportive of the signaling – in the absence of the Langevin behavior, energy can become

trapped and the damping to give the fully oriented, reoriented chain is never perfect. Therefore this is a robust signaling mechanism at high temperatures. As opposed to some of the previous work we have reported, that would only really work in the limit in which damping and thermal effects are relatively small compared to the coherent, energy conserving behaviors.

We've also studied switch times (Figure MR2). We find that the switch times as a function of the length fit very nicely to an exponential – therefore the process is good for finite time switching only for relatively short strands. Very long strands will nevertheless switch extremely effectively, but they would simply take a great deal longer.

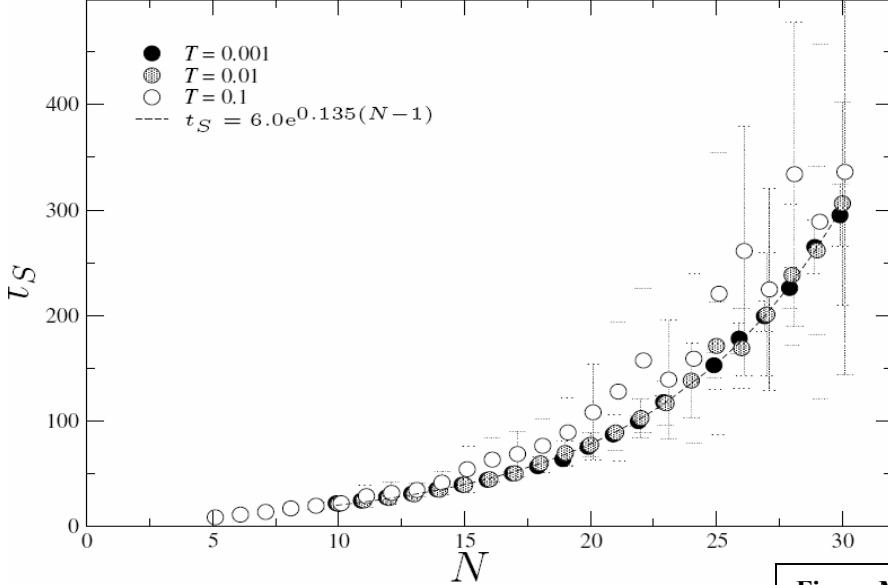
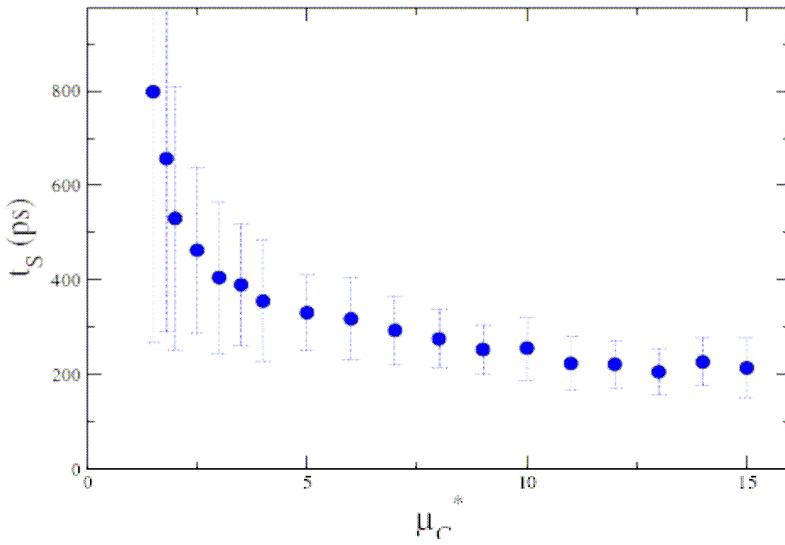


Figure MR2. Switching time from Langevin simulations. Upper shows dependence on temperature and on chain length, lower shows



We also calculated thermal dependence, friction dependence and other interesting behaviors. Finally, simulation of propagation through a curved chain or a kinked chain (Figure MR3) once again demonstrates that these dipolar propagations can be quite robust –so long as the radius is relatively small, or the kink angle is below roughly 22° , we observed that the transport and reorientation are, again, totally effective.

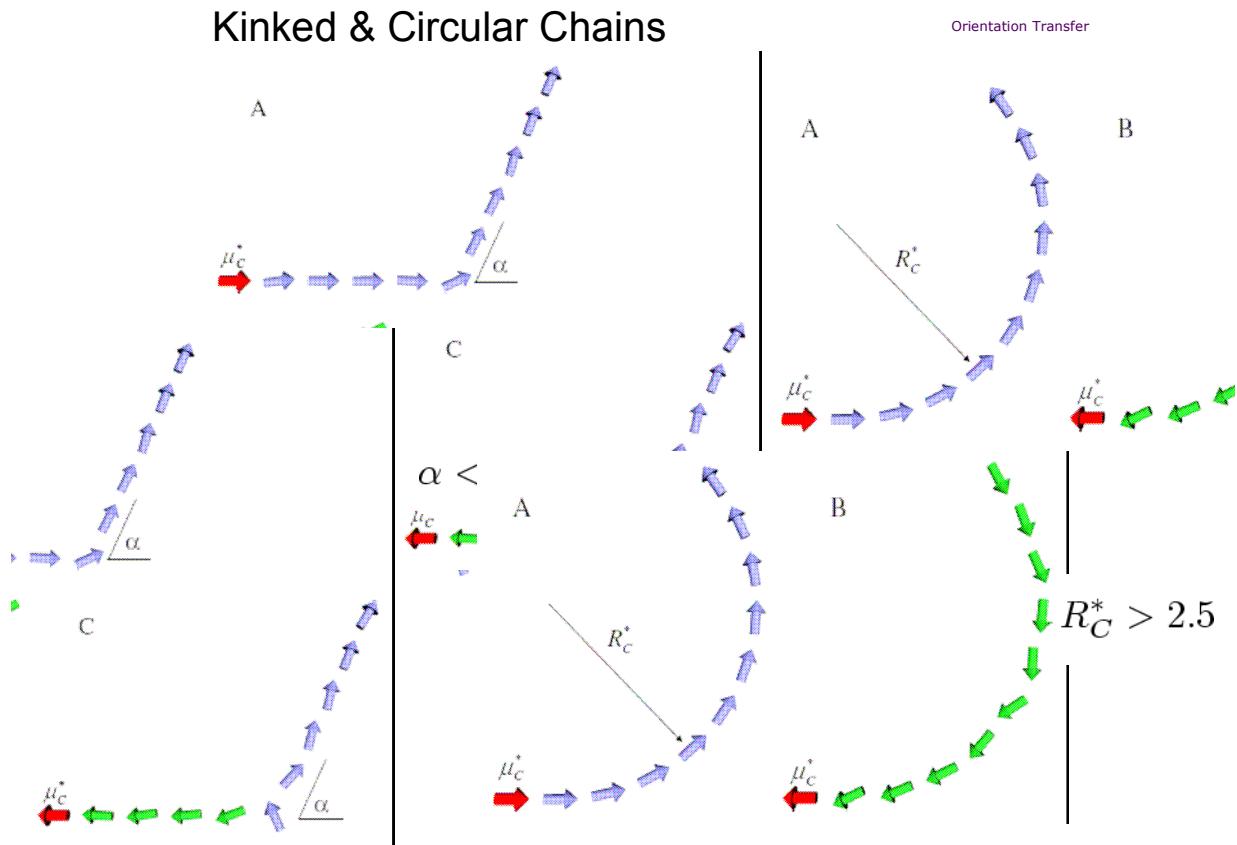


Figure MR3. The control dipole (red) can change the orientation of the whole line of dipolar species, even if it is kinked or circular.. This allows a very efficient modality for switching and signaling in linear rotor chains.

MICHL CONTRIBUTION

The Michl group accomplished work in four areas: (i) synthesis of rotor molecules, (ii) attachment chemistry and characterization of rotors on surfaces, (iii) detection of internal rotation in surface mounted rotors, and (iv) computer simulations of surface-mounted rotors.

(i) *Synthesis of rotor molecules.* The work has been directed toward two types of targets: new altitudinal rotors and new azimuthal rotors. The preparation of nine different rotors, four altitudinal and three azimuthal have been completed, and two others are well advanced.

The first altitudinal rotors synthesized used support stands based on tetraphenylcyclobutadienecyclopentadienylcobalt double decker sandwich complexes designed to be attached to a gold surface through ten sulfur-containing tentacles or to quartz surfaces through trialkylsiloxane groups. Both dipolar, **1** (Figure JM1), and non-polar, **2** (similar to Fig. JM1 except with H instead of F), rotors have been synthesized. The dipole in rotor **1** was incorporated so that the rotor could be made to flip by a strong electrostatic field. We were able to mount these rotors on atomically flat Au(111), image them by scanning tunneling microscopy (STM) and induce flipping of dipolar rotors by the application of a static electric field of the STM tip.

Three other altitudinal rotors, all with triptycene-based rotators carrying three paddles, were completely or partially synthesized. One is the first molecular rotor ever constructed using self-assembly, based on Pt coordination chemistry. This is one of the first times metal ion based self-assembly has ever been used in targeted synthesis of any functional structure, and the simplicity of

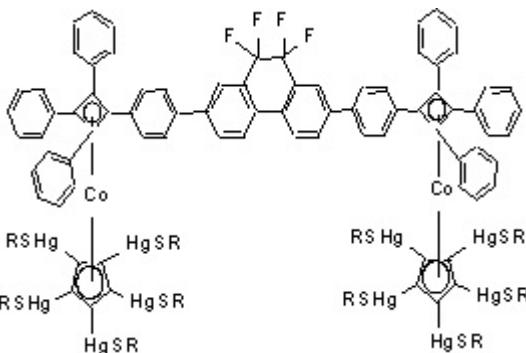


Figure JM1. Dipolar altitudinal rotor **1**, R = $(\text{CH}_2)_2\text{SMe}$.

the process that leads to a fairly complex structure is striking (Figure JM2). We believe that this accomplishment opens the door to the future synthesis of many functional structures of rotors and other objects for nanotechnology. The incomplete synthesis of a high-clearance altitudinal rotor molecule, which relies on classical approaches and is much more laborious, is well advanced but not yet finished (Figure JM3). It is a generalization of the second-generation low-clearance altitudinal rotor that we have completely synthesized (Figure JM3A).

A set of two azimuthal rotors carry rotators composed of two paddles, which contain a chromophore whose lowest excited

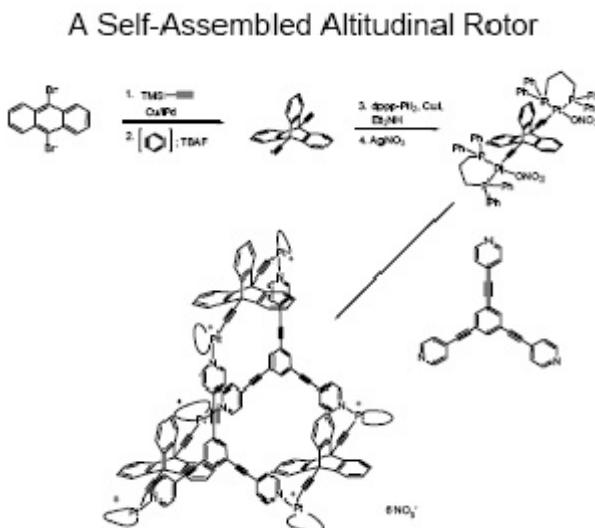


Figure JM2. Synthesis of a self-assembled rotor.

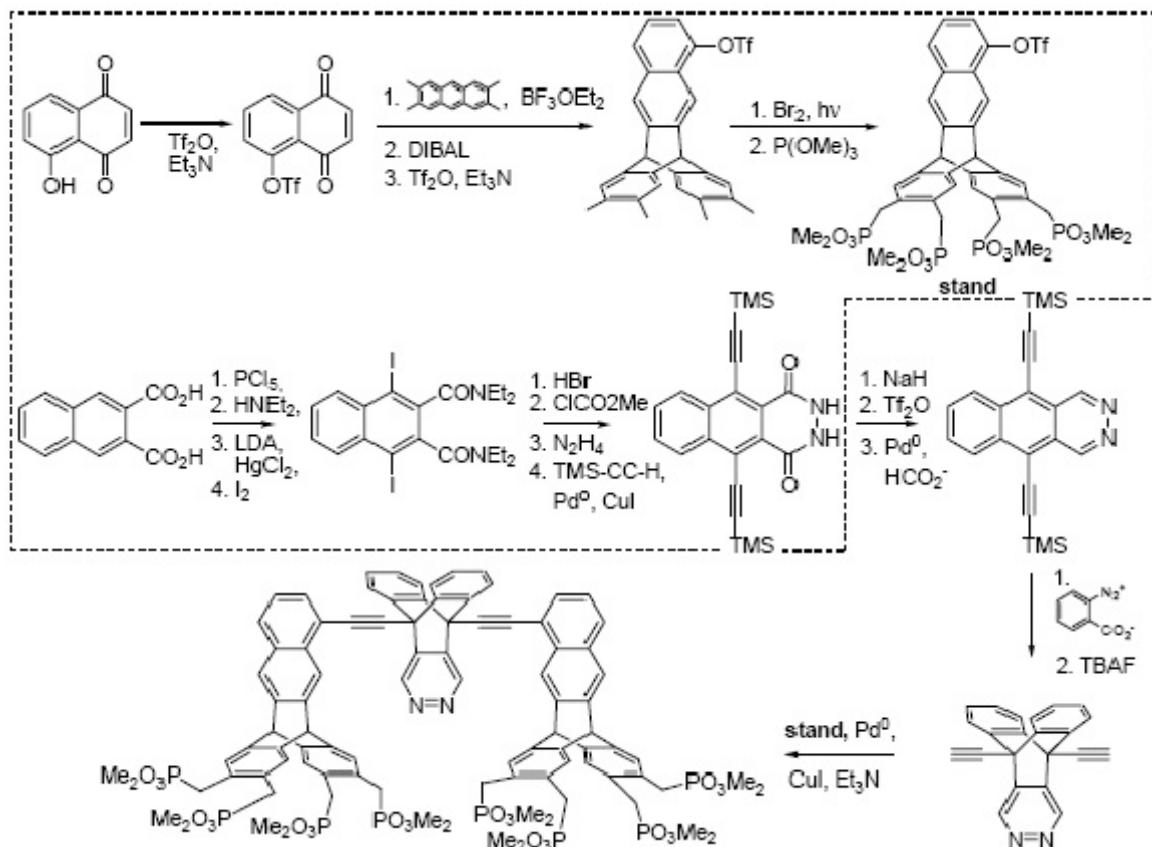


Figure JM3. The framed part of the synthesis has been accomplished.

state transition moment is directed perpendicular to the rotor axle were designed and synthesized for time-dependent fluorescence anisotropy measurements. The one whose synthesis has been completed is shown in Figure JM4. Since a study of its properties after surface mounting revealed that its axle does not mount perpendicular to the surface and that the structure therefore is unsatisfactory (see below), a new principle for the mounting of azimuthal rotors has been developed, with long fatty acid chains serving as feet for anchoring the rotor molecule inside a Langmuir-Blodgett film. The model compound with a naphthalene chromophore has been made (Figure JM5) and after successful testing, the synthesis of a rotor molecule was initiated but has not yet been completed (Figure JM6).

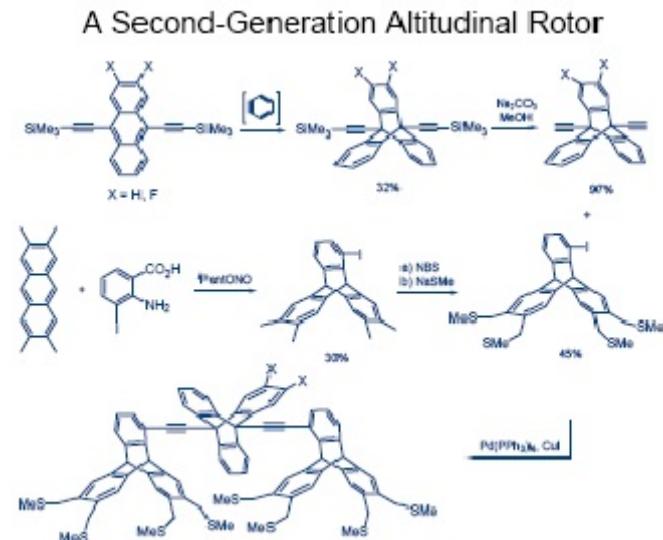


Figure JM3A. Synthesis of the second-generation altitudinal rotor.

(ii) *The study of rotor attachment chemistry and the characterization of surface-mounted rotors.* This work focused on quartz and gold surfaces. After considerable effort, attachment chemistry protocols for the first generation altitudinal rotor on quartz surfaces were established, leading to well-characterized film samples

suitable for dielectric spectroscopy measurements in the laboratory of Prof. Laura Clarke at North Carolina State physics department. Figure JM7 shows the dispersion of the Debye peak due to the motion of the rotator dipole.

On gold, STM images have been obtained for many rotor molecules, and as an example, results for the self-assembled rotor of figure JM2 are given in Figure JM8. Analysis of high resolution XPS data(exemplified for a new surface mounting procedure in Figure JM9)

for various gold-surface-mounted rotors obtained from a collaboration with colleagues in the Czech Republic has yielded a much better understanding of the stability and nature of attachment

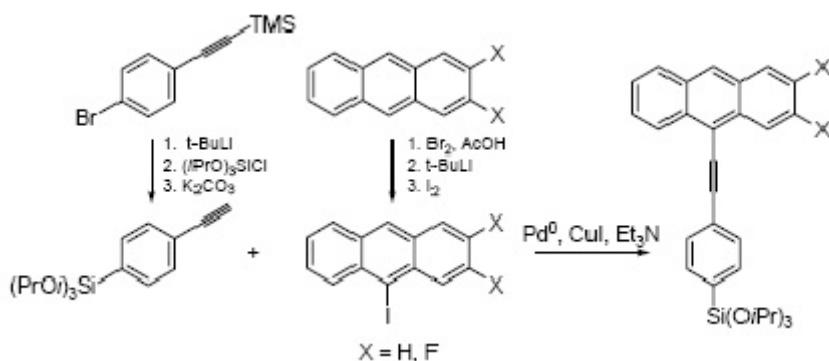


Figure JM4. Synthesis of an azimuthal rotor.

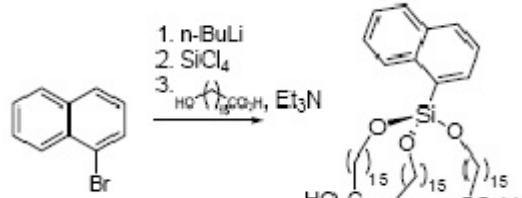


Figure JM5. Synthesis of a test molecule

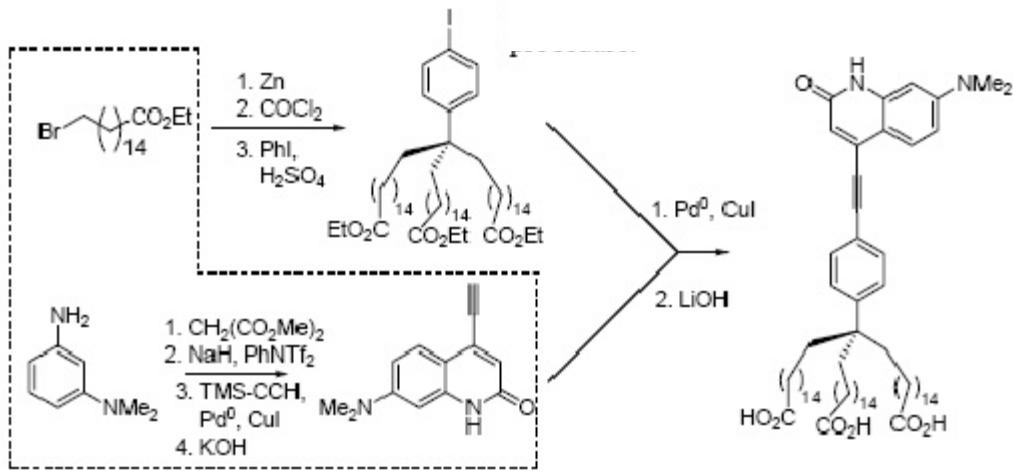


Figure JM6. The framed part of the synthesis has been accomplished.

chemistry of Hg

and sulfur containing moieties. Tentacles containing only Hg have been discovered to be sufficient for tethering molecules to surfaces under some conditions, and this discovery may have important implications for the attachment of molecules to metals in general. Sulfur containing tentacles were found to be stable in ambient conditions for only a few hours, but the rotor remains attached to the surface through its mercury atoms.

The measurement of the total mass of a rotor film on Au by quartz crystal microbalance techniques was attempted but did not lead to useful results because of system instabilities.

An electrochemical Langmuir trough has been developed (Figure JM10) and is in use for the development of techniques for the construction of molecular rotor grids on mercury surface. A

trigonal connector for making hexagonal grids **3** was investigated and found to be conveniently absorbed or desorbed through electrochemical control with surface-potential dependent molecular spacings (Figure JM11). There are indirect experimental indications that a hexagonal grid has been synthesized on the trough (Figure JM12).

With Harrick, Inc., we have developed and published a highly sensitive method for taking IR spectra of molecules on metal surfaces (“pseudo-ATR”). This was used for the study of surface-mounted rotors.

(iii) *Detection of rotation.* The anthracene-containing azimuthal rotor whose synthesis is shown in Figure JM4 was deposited on a very flat quartz surface cleaned and treated in a special way. It was diluted on the surface with another silane to avoid aggregation and energy transfer in fluorescence experiments. Even under optimal conditions, no evidence for axle alignment perpendicular to the surface was obtained. The same disappointing result was obtained for two other rotor molecules, with naphthalene and 2,3-methylenedioxy chromophores (formulas not shown). Rotor alignment and minimal energy transfer are necessary conditions for the intended polarization anisotropy decay experiments that will allow for the detection of thermally induced internal rotation.

A better procedure was developed for surface mounting that actually produced alignment under conditions of considerable dilution. This is based on an adaptation of the Langmuir-Blodgett film method to rotor films. Chromophoric azimuthal rotors with three octadecyl fatty acid legs have

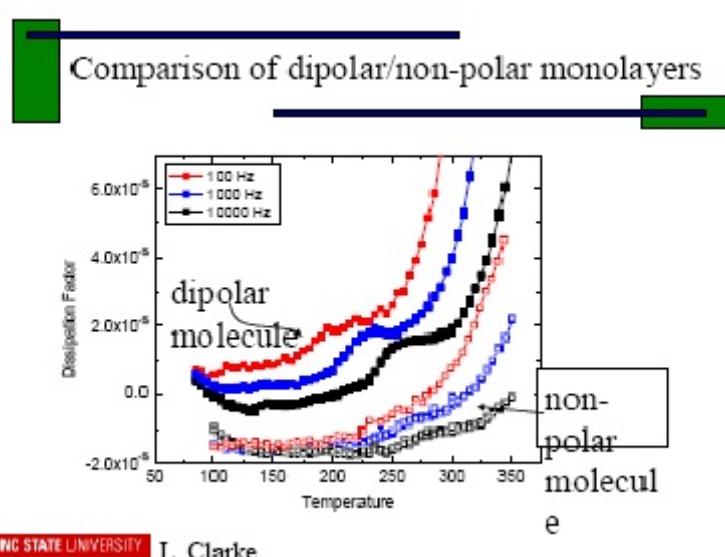


Figure JM7. L. Clarke's dielectric spectroscopy measurements

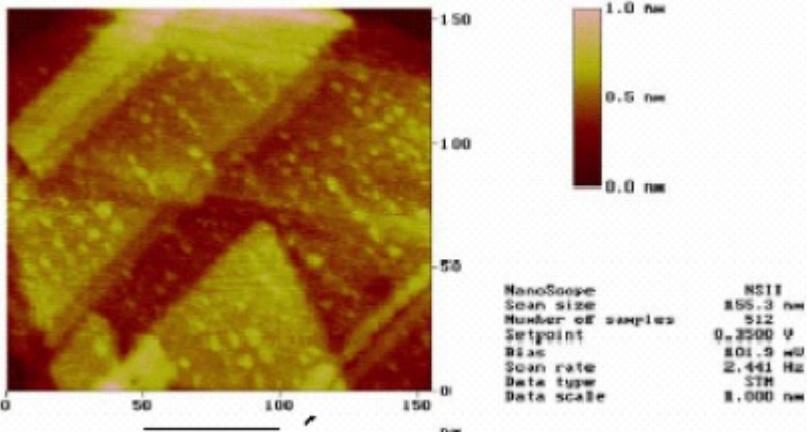


Figure JM8. STM of the rotor of Figure JM2 mounted on Au(111).

XPS of Dipolar Rotor on Au(111)

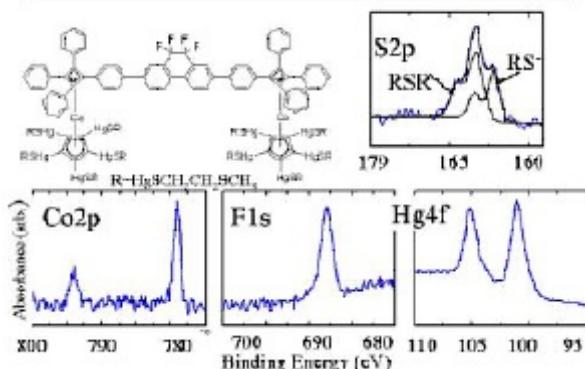


Figure JM9. XPS results for first-generation altitudinal dipolar rotor on Au(111).

been synthesized and found to make excellent Langmuir-Blodgett films (Figure JM13) that can be transferred to quartz or Si(111) substrates and

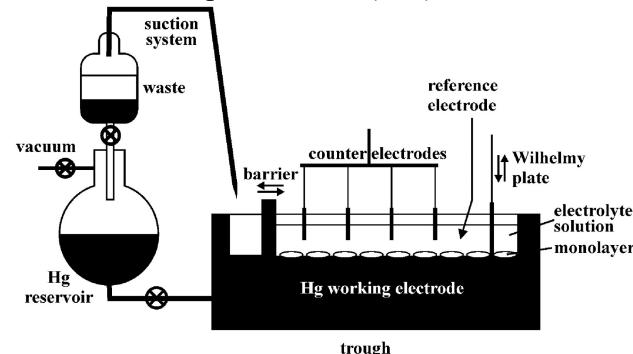
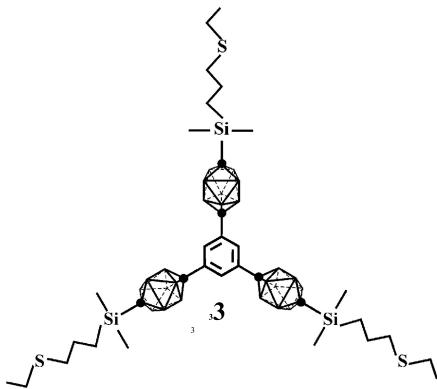


Figure JM10. Schematic drawing of the electrochemical Langmuir trough.



produce a ~40 degree average deviation of the rotator axle in both neat and dilute films (Figure JM14).

For the first-generation altitudinal rotor **1** it has been demonstrated that it flips its orientation spontaneously at room temperature or intentionally by a strong electrostatic field. We were able to mount these rotors on atomically flat Au(111), image them by scanning tunneling microscopy (STM) and induce flipping of dipolar rotors by the application of a static electric field of the STM tip. The conformation of the molecule, i.e. the orientation of the dipole, was detected by differential barrier height imaging spectroscopy (DBHI), a method developed by us. Ordinary BHI is a map of the local work function variation of a surface. The work function of a metal is the amount of energy needed to remove an electron from its surface to

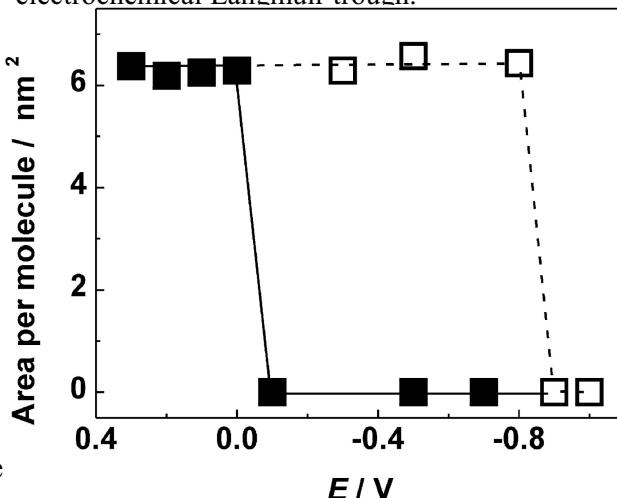


Figure JM11. Molecular surface areas extrapolated to zero pressure, as a function of applied potential. Hollow squares represent the results of measurements in which the monolayer was formed

at +0.1 V and then compressed at the potential or intentionally by a strong electrostatic field shown.

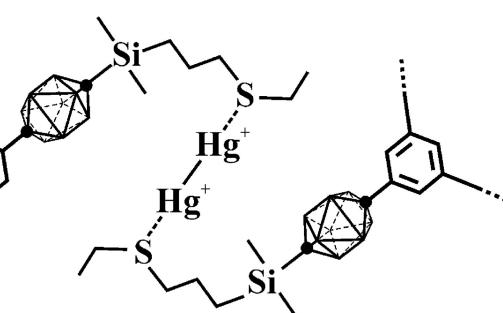


Figure JM12. Most probable structure of a hexagon edge in the proposed hexagonal network of Hg²⁺ cations.

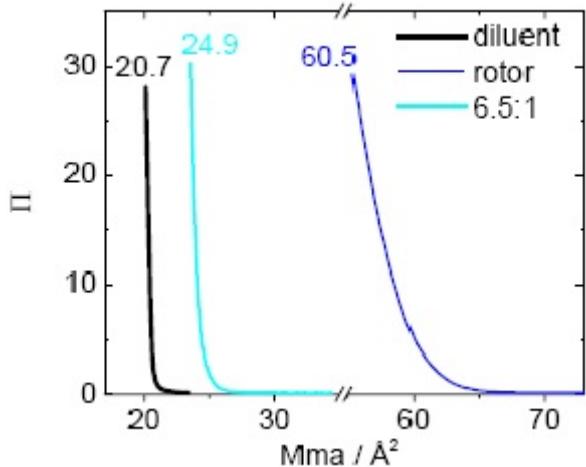


Figure JM13. Langmuir-Blodgett isotherms of the rotor of figure JM5 diluted with stearic acid.

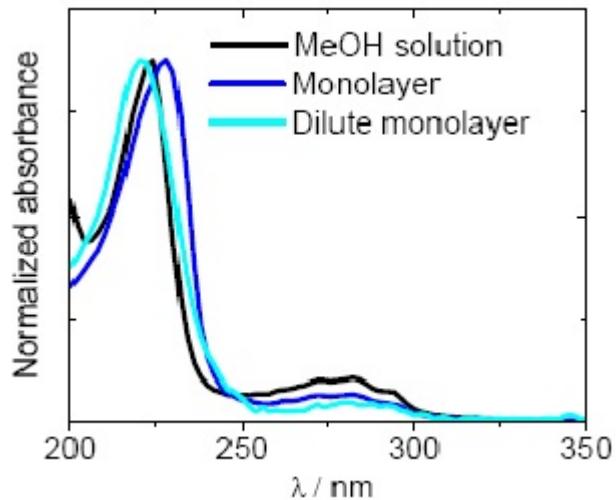


Figure JM14. UV absorption of the rotor of Figure JM5 in a monolayer and in isotropic solution.

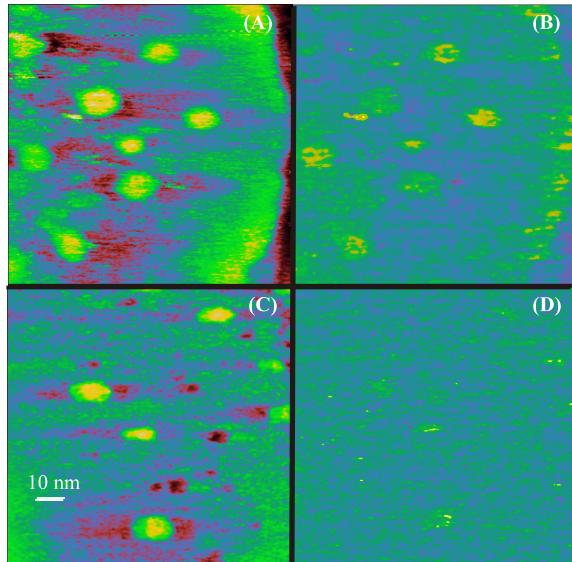


Figure JM15. Current mode (200 pA, 200 mV) STM (A, C) and DBHI (B, D) images of **1** (top) and **2** (bottom) on Au(111). Six colors (black, maroon, blue, green, yellow, and white) divide the vertical range (left, 0-1 nm; right 0.0-0.2 V).

increased. The local work function of a surface is strongly affected by adsorbates and especially, by surface dipoles. The local work function is measured, in our system, by modulating rapidly at 5 kHz by a small amount (0.3 Å) the distance z of the tip from the surface. This causes the tunneling current i to be modulated at the same frequency, and both the current and its derivative di/dz are measured (Figure JM15). Since i falls off exponentially with z , so does di/dz . The proportionality constant that relates i and di/dz is equal to $-\beta\varphi^{1/2}$, where β is a known constant and φ is the combined work function of the surface and the tip. The presence of a permanent dipole in an adsorbate will infinity. The physics behind this measurement relies on the fact that the easier it is to remove an electron from the surface, the farther out into vacuum will its wave function extend, and the slower will be the fall off or the tunneling current to the tip as z is increased. The local work function of a surface is strongly affected by adsorbates and especially, by surface dipoles. The local work function is measured, in our system, by modulating rapidly at 5 kHz by a small amount (0.3 Å) the distance z of the tip from the surface. This causes the tunneling current i to be modulated at the same frequency, and both the current and its derivative di/dz are measured (Figure JM15). Since i falls off exponentially with z , so does di/dz . The proportionality constant that relates i and di/dz is equal to $-\beta\varphi^{1/2}$, where β is a known constant and φ is the combined work function of the surface and the tip. The presence of a permanent dipole in an adsorbate will

Differential Barrier Height Measurement: 2nd Generation Dipolar Rotor

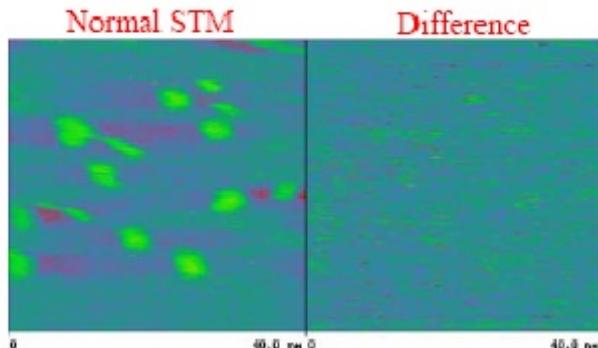


Figure JM16. Ordinary STM and DBHI of the rotor of Figure JM3A on Au(111).

increase the local work function if its negative end is turned away from the surface and decrease it if the negative end faces the surface. The application of an electric field on the order of 1 V/nm is sufficient to lock the dipole in the field direction against room-temperature thermal motion. In our DBHI measurement, we raster the tip in the constant-current mode, but go over each line twice, once with each field polarity. When the field holds the negative end of the rotator dipole close to the surface, we measure $\varphi_+^{1/2}$, and when it is far from the surface, we measure $\varphi_-^{1/2}$. Fig. JM15 (top) shows an ordinary STM image of the dipolar rotors on Au(111) along with its DBHI plot. Rotors that show up as bright spots in the DBHI plot have work functions that depend on the direction of the applied field and therefore are the ones that have undergone a rotational conformation change to reorient their dipole with the field. The same is shown in Fig. JM15 (bottom) for the non-polar rotor in a control experiment. Only very weak bright spots are observed from induced dipoles, consistent with the absences of reorientable dipoles in these rotors. Repeated scans of the same field of dipolar rotors shows blinking in the differential images. We attribute this to temporary rotor blockage caused by the tentacles.

The initial DBHI measurements that showed rotor motion in the first generation altitudinal rotor **1** suffered from poor resolution and interfering thermal motion of the attachment tentacles. To circumvent these problems the measurements were retried by the Boulder student Mary Beth Mulcahy on the low-temperature high vacuum STM instrument in Hersam's laboratory at Northwestern University. These experiments produced no improvement because of contamination of the film by an adventitious surface layer of water. Conditions for removal of this contamination by vacuum bake out are under investigation but so far heat treatment has only led to removal of the rotors from the gold surface.

The second generation altitudinal rotor of Figure JM3A was also investigated by the DBHI method using the ambient STM instrument. The DBHI signal shows no apparent internal rotary motion when probed by the STM tip (Figure JM16). Possible explanations for

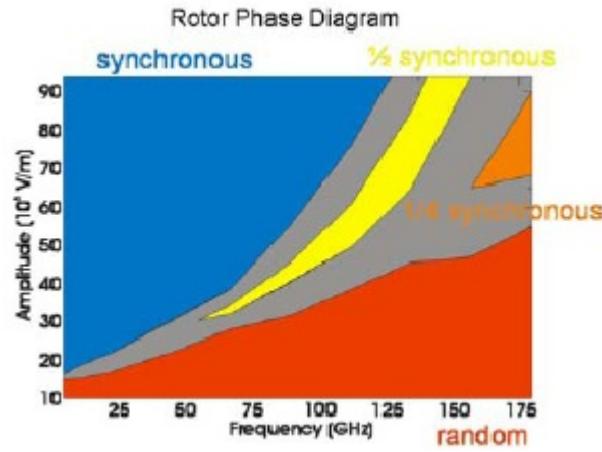


Figure JM17 Phase diagram at 10 K of the rotor **1** mounted on Au(111) obtained by molecular dynamics simulation.

Thermally Activated and Driven Unidirectional Rotation

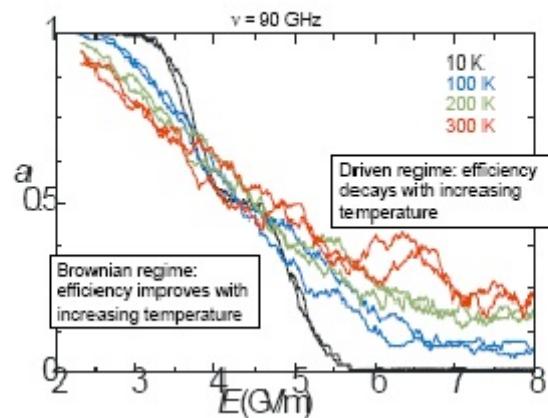


Figure JM18. Molecular dynamics simulation of the unidirectional rotation in the first generation rotor **1** mounted on an Au(111) surface by electric field normal to the surface and oscillating at 90 Ghz. The probability of skipping a cycle of the driving field is shown as a function of the field strength at a series of temperatures.

this observation include having the rotor stand knocked on its side by the passage of the tip. The second generation rotor is anchored only at eight points, whereas the first generation rotor that did show internal rotary motion by DBHI was anchored at forty points.

(iv) *Computer simulations.* From simulations of flow-driven altitudinal rotors, it has been concluded that for efficient rotation a rigid structure is necessary and that design that we have been using probably does not meet this criterion. Smaller and presumably much more rigid rotors have been considered and modeled.

Continued simulations of the first generation altitudinal rotor¹ produced a phase diagram of its unidirectional rotational response to oscillating electric field at low temperature as a function of field amplitude and frequency (Figure JM17). They revealed conditions for a subharmonic response in which the surface-mounted molecule acts as a parametric oscillator and turns at one-half or even only one-quarter of driving field frequency. The two regimes of operation, thermal(Brownian) and driven, are clearly distinguished by their different response to a temperature increase (Figure JM18).

A light-powered rotor molecule (Fig. JM.19) that contains a paddlewheel on an axis that is the edge of a trigonal prism was designed. Molecular dynamics simulations that suggest that the absorption of a photon of light causes the rotor to make half a turn in the course of a few picoseconds, soon thereafter completed to a full turn. A train of light pulses is predicted to induce a fast and steady unidirectional rotation of the rotor, which could be used to propel a thin layer of a fluid along a surface if the rotors were mounted in an organized array ("molecular pump"). The underlying principle is charge separation upon excitation followed by electrostatic attraction of the now positively charged donor (one of the paddles on the wheel) to the now negatively charged acceptor (located asymmetrically next to the paddlewheel), and thermal relaxation to the starting position. The structure has been designed in a way that favors unidirectional motion.

We conceived a molecule with a rotating group containing an electron donor (or acceptor) and a static part containing an electron acceptor (resp. donor). Then, upon excitation, an electron transfer would quickly occur.

The charge separation would then cause electrostatic attraction of the now positively charged donor to the now negatively charged acceptor. This is the driving force for the rotation. This power stroke would then be followed by a thermal relaxation to the starting position. The trick is to engineer the potential energy surfaces for the rotation coordinate to favor unidirectionality in both the driven and thermal steps. The structures are based on similar albeit simpler molecular rotor structures recently synthesized in our group.

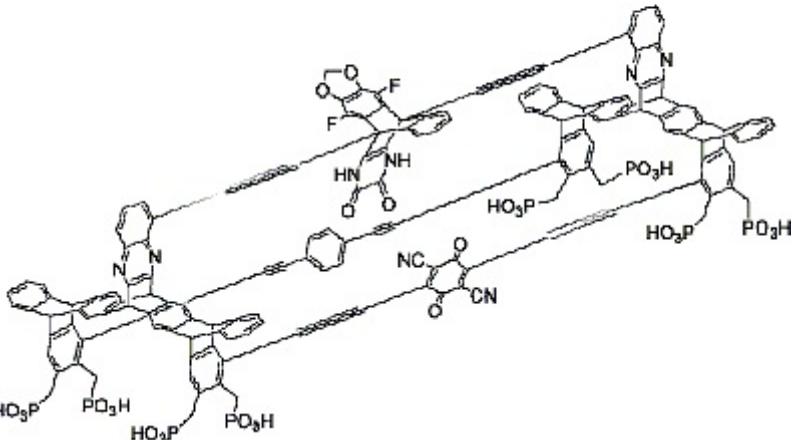


Figure JM19. Proposed structure of light-driven rotor.

The desired ground and excited state rotation potential surfaces are shown in Fig. JM20.

Each state has only one minimum and one maximum. The rotation angle of the maximum on the excited state surface needs to be shifted with respect to the ground state minimum so that after excitation the system geometry “always” relaxes by rotating the rotator in the same sense (left in Figure JM20). Similarly the excited state minimum must be shifted in the same direction with respect to the ground state maximum so that after electronic relaxation the system geometry relaxes by rotating the rotor in the same sense thus fulfilling a full turn.

To study the dynamics of the rotor we implemented some new features into the TINK program. A customized molecular dynamics simulation program and a universal force field were used in the calculations. To design an optimal light driven rotor we used the rotational surface as a guide. An example is shown in Fig. JM20. The power delivered in each cycle is ~ 20 kcal/mol, which is only a fraction of the photon energy. A series of MD simulations was then performed for the optimal rotor structure. After some initial equilibration at 300 K the molecule is switched from ground to excited surface (the charge distribution changes), simulating a light absorption event, and the dynamics is propagated further. Typically, within just a few picoseconds the system reaches the minimum geometry in the excited state. After ~ 20 ps the molecule is returned to its ground state potential again. The system then undergoes thermal relaxation to its ground state minimum geometry. It has a choice of rotating in the same sense in which it turned in the excited state, or returning back in the opposite sense. The molecule chooses the desired unidirectional motion only $\sim 70\%$ of the time, and the design clearly needs further improvement. It seems that the direction of the thermal relaxation step depends strongly on the geometry at the very moment when the electron returns.

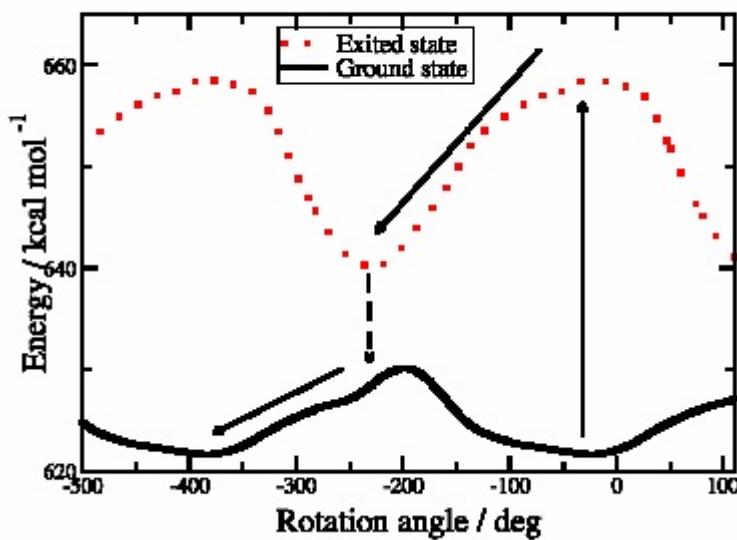


Figure JM20. Ground and excited-state rotational potential surfaces.